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New directions in mechanics

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Abstract

The Division of Materials Sciences and Engineering of the US Department of Energy (DOE) sponsored a workshop to identify cutting-edge research needs and opportunities, enabled by the application of theoretical and applied mechanics. The workshop also included input from biochemical, surface science, and computational disciplines, on approaching scientific issues at the nanoscale, and the linkage of atomistic-scale with nano-, meso-, and continuum-scale mechanics. This paper is a summary of the outcome of the workshop, consisting of three main sections, each put together by a team of workshop participants.

Section 1 addresses research opportunities that can be realized by the application of mechanics fundamentals to the general area of self-assembly, directed self-assembly, and fluidics. Section 2 examines the role of mechanics in biological, bioinspired, and biohybrid material systems, closely relating to and complementing the material covered in Section 1. In this manner, it was made clear that mechanics plays a fundamental role in understanding the biological functions at all scales, in seeking to utilize biology and biological techniques to develop new materials and devices, and in the general area of bionanotechnology. While direct observational investigations are an essential ingredient of new discoveries and will continue to open new exciting research doors, it is the basic need for controlled experimentation and fundamentally-based modeling and computational simulations that will be truly empowered by a systematic use of the fundamentals of mechanics.

Section 3 brings into focus new challenging issues in inelastic deformation and fracturing of materials that have emerged as a result of the development of nanodevices, biopolymers, and hybrid bio–abio systems.

Each section begins with some introductory overview comments, and then provides illustrative examples that were presented at the workshop and which are believed to highlight the enabling research areas and, particularly, the impact that mechanics can make in enhancing the fundamental understanding that can lead to new technologies.
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1. Section 1: self-assembly and fluidics: from building blocks to functional systems and beyond [3]

1.1. Introduction

Structures form spontaneously at all size scales (Ball, 1999). Electrons, protons and neutrons form atoms. Atoms form clusters and molecules. These building blocks form mesostructures; examples range from the classic Guinier–Preston zones in aluminum–copper alloys (Gayle and Goodway, 1994), to ubiquitous lipid bilayers, and to more recently discovered strain-induced quantum dots (Leonard et al., 1993). Daoud and Williams (1999) have edited a lucid introduction to objects under the rubric of soft matter, such as block copolymers, surfactants, colloids, emulsions, and liquid crystals. Other self-assembled mesostructures include nanohole arrays formed by the anodic oxidation of aluminum (Masuda and Fukuda (1995), droplet lattices formed from a liquid film (Chou and Zhuang, 1999; Schaffer et al., 2000), dealloying nanoporous structures (Erlebacher et al., 2001), and magnetic dots on an insulating substrate (Gai et al., 2002). We are, of course, aware of larger self-assembled structures: animals and plants, rivers and mountains, stars and galaxies.

Life, the most complex self-assembly currently known, by its very existence offers inspiration. The ultimate self-assembled structures will be multifunctional, simultaneously transporting energy, matter and information. Fluidics will be an integral part of those structures, in addition to solid state components. The structures will have the attributes of self-preservation: healing, self-sensing, and replication. They will be adaptive and tunable, and be programmed to self-de-assemble. Hierarchical organization is needed to achieve these goals.

Self-assembly and directed self-assembly (Heller and Guttman, 2002; Section 10.7) will be an increasingly significant part of the technology that mass-produces devices that harvest energy, sense

[3] Prepared by S. Granik, Z. Suo (coordinator), S. Torquato, and F. van Swol.

trace amounts of matter, and manipulate information. Molecular cars may one day be self-assembled and outperform the protein motors in nature, with higher energy transduction efficiency and greater versatility. The state of the art is of course not so advanced: the gap between quantum dots and life is huge. This gap can only be filled by inspiration and perseverance in years to come.

Edisonian-type investigations have been driving many, if not all, of the most exciting advances in this important area of research. Neither our understanding nor our control of self-assembly is adequate to map out the road to the ultimate structures that will, one day, achieve selectivity and functionality of the kind that is already achieved routinely by the lowliest forms of living organisms. While many systems self-assemble, too few have led, by rational design, to profoundly new technological uses. It is an exciting time when both Edisonian and mechanistic approaches can make great progress.

We next describe several current research topics in which the mechanistic approach plays a significant role in understanding and exploiting mesoscale self-assembly and fluidics. In the space available, we will only describe a few examples. A notable omission is strain-induced quantum dots, a subject to which mechanics has made crucial contributions (Freund and Suresh, 2003; Gao and Nix, 1999; Shchukin and Bimberg, 1999). Also missing is a more general topic: nanofabrication; see, e.g., Decher and Schlenoff (2003) and Heller and Guttman (2002). Several mechanical-based fabrication processes have shown astonishing capabilities (Xia et al., 1999; Marrian and Tennant, 2003). For example, Chou et al. (1995) showed that embossing print can replicate nanoscale features, which can then be used as templates to make functional structures, such as nanoscale transistors. The revelation has inspired worldwide activities to retool this ancient technology, embossing print, for modern uses. As another example, Alaca et al. (submitted) have developed a method to introduce a controlled pattern of cracks, which can be used as fluid channels or as templates to form nanowires. Mechanics has long played a significant role in manufacturing technologies, such as metal forming, ceramic sintering, and polymer molding. Nanofabrication involves deformation, fracture, and mass transport at the nanoscale, and will be a persistent challenge to mechanics in the coming decade.

1.2. Evaporation-induced self-assembly (EISA)

Evaporation-induced self-assembly (EISA) illustrates the enormous versatility of self-assembly (Fig. 1). Start with a dilute aqueous solution of alcohol, amphiphile and Si-precursor. Allow water and alcohol to evaporate. When amphiphile exceeds a critical concentration, micelles form in lamellar, hexagonal and cubic phases. The micelles are the templates for silica structures by condensation reactions. EISA can be implemented in many ways: spin coating, spray drying and dip coating. During dip coating (Lu et al., 1997), for example, evaporation is extremely fast at the leading edge (the top). The assembly progresses by nucleation at the top and growth toward the bottom, like a zipper. Large defect-free domains of various phases emerge. EISA is a deceptively easy route to highly intricate structures. By including other ingredients in the aqueous solution, one can explore an enormous range of nanocomposites.

EISA poses a great challenge to fundamental understanding. Viewed from this angle, the dip coating is a complex process. New length scales emerge as the structures form. Such a process cannot be described by conventional constitutive relations. The viscosity, evaporation rate, solution vapor surface tension are all complex functions of the concentrations. EISA can be visualized as a trajectory in the equilibrium phase diagram of an amphiphile–ethanol–water system. This first-order approach provides insight into which structures may be encountered. However, the two interfaces, liquid/vapor and liquid/substrate, can modify the relative stability of various structures. So can kinetic factors such as shear and concentration gradients across the films. Incidentally, the liquid/substrate interface presents a good illustration of directed assembly. By controlling the substrate, one may harness the inherent self-assembling tendencies of the solution and steer the structure formation process into desirable directions.

Modeling of amphiphile self-assembly is an active field (e.g., Morozov and Fraaije, 2001; Rankin

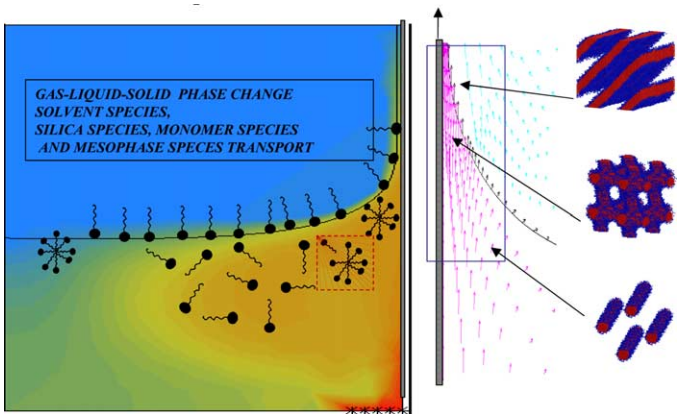

Fig. 1. Schematic illustrating evaporation-induced self-assembly (EISA) for the dip-coating process. A substrate is dipped into an aqueous solution of surfactant and silica precursor. Surface tension causes a thin film to adhere to the substrate as it is pulled upwards. Fast evaporation at the leading edge of the film causes rapid concentration of the surfactant, which produces three-dimensional structures inside the thin film. These 'soft' organic structures then serve as templates for the inorganic architectures of various symmetries. (Courtesy of R. Schunk and A.C. Sun of Sandia National Laboratories).

et al., 2001). An obvious challenge is the significant time and length scale variations during self-assembly. One needs to capture molecular level detail in some form, in order to capture the effects of amphiphile size, for instance. One must also allow for larger length scale phenomena in order to represent, say, the formation of periodic structure, the role of interfaces, shear, or the concentration gradients. To fully model the dip coating process requires the implementation of a multilength scale strategy that reaches from molecular to continuum.

Various molecular modeling approaches are currently pursued to study aspects of self-assembly, including molecular dynamics (MD), Monte Carlo (MC), and density functional theory (DFT), as well as hybrid forms of these. Some of these studies involve lattice models while others are off-lattice. A new approach, introduced by Fraaije (1999), involves a coupling of DFT with transport equations. This mesoscopic approach has been very successful in modeling actual processes, illustrating the role of process variables such as shear as well as the need for coarse-graining of molecular features. A coupling of MC (or DFT) with concentration gradients and chemical reactions has also been introduced (Malanoski and van Swol, 2002), further expanding the arsenal of the process variables available.

With relative ease, EISA can be used to apply coatings to other materials. An interesting application involves mimicking the Lotus Leaf. High solid–liquid interfacial energies, in conjunction with rough surface topographies, cause high contact angles, rolling and bouncing of liquid droplets, and self-cleaning of particle contaminants (Mahadevan and Pomeau, 1999; Quéré, 2002; Granick et al., 2003). When a fluid channel has such a superhydrophobic coating, one observes increased flow rates (reduced friction coefficients), significant slip velocities, and large slip-lengths. Implications for energy-efficient fluidics are profound.

1.3. Self-assembly, statistical mechanics, and materials optimization

To accelerate future achievements, it is important to supplement experimental approaches with emerging statistical–mechanical techniques that have yet to be fully exploited (Torquato, 2002). Typically, interest has been focused on finding the structure and macroscopic properties of many-body systems given the interactions—what we refer to as the "forward" problem of statistical mechanics. The "inverse problem" provides a systematic statistical–mechanical methodology to find the interaction potentials in many-body systems of particles that lead spontaneously to a prescribed or

"target" structure (Stillinger et al., 2001). Existing work in this direction is limited. For example, we still do not know the class of structures that can be achieved by a spherically-symmetric pair potentials, not to mention anisotropic pair potentials or higher-order multibody interactions.

This is clearly fertile territory for further investigation. These ideas and results can be tested experimentally using colloidal systems of particles, since both repulsive and attractive interactions can be manipulated (e.g., particle surface modification and/or the addition of electrolytes to the suspension). This "inverse" approach holds great promise to control self-assembly in many-particle systems to a degree that surpasses the less-than-optimal path that nature has provided. Indeed, we envision being able to "tailor" potentials that produce varying degrees of disorder, thus extending the traditional idea of self-assembly to incorporate both amorphous and crystalline structures, as well as quasicrystals using the recent notion of order metrics (Kansal et al., 2002). Thus, this inverse approach has important implications for the systematic design of new materials.

The idea of tailoring potentials to generate targeted structures is motivated by the rich array of fundamental issues and questions offered by this fascinating inverse statistical–mechanical problem, as well as our recent ability to identify the structures that have optimal bulk properties or desirable performance characteristics. The latter includes novel crystal structures for photonic band-gap applications (Ho et al., 1990), materials with negative or vanishing thermal expansion coefficients (Sigmund and Torquato, 1996), materials with negative Poisson ratios (Xu et al., 1999), materials with optimal transport and mechanical properties (Hyun and Torquato, 2001), mesoporous solids for applications in catalysis, separations, sensors and electronics (Ferey and Cheetham, 1999), and multifunctional materials (Nemat-Nasser, 2002; Torquato et al., 2002).

Employing multifunctional optimization techniques, it has recently come to light that triply periodic two-phase bicontinuous composites with interfaces that are the Schwartz simple cubic and diamond minimal surfaces (see Fig. 2), are not only geometrically extremal but extremal when there is a competition between electrical conduction and thermal conduction (Torquato et al., 2002). These two-phase composites are bicontinuous in that the surface (two-phase interface) divides space into two disjoint but intertwining phases that are simultaneously continuous. Triply periodic minimal surfaces arise in cell membranes and other biological formations. Since biological systems must be able to perform a variety of functions well, this suggests that such structures would be mechanically stiff even if one of the phases is a compliant solid or a liquid, provided that the other phase is a relatively stiff material. Indeed, the multifunctionality of such two-phase composites has been further established by showing that they are also extremal when a competition is set up between the effective bulk modulus and electrical (or thermal) conductivity of the composite (Torquato and Donev, in press). This example offers a glimpse into the fascinating and rich types of microstructures that can result when different functionalities compete against one another. We

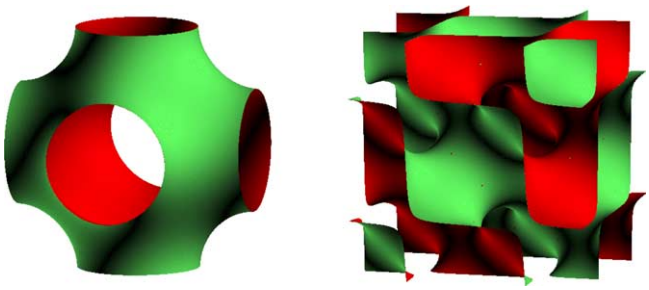

Fig. 2. Unit cells of two different minimal surfaces: (left panel) Schwartz simple cubic surface and (right panel) Schwartz diamond surface (Torquato et al., 2002).

are far from understanding multifunctionality from a first-principles point of view.

1.4. Molecular assembly on solid surfaces

The invention of the scanning tunneling microscope (STM), in the 1980s, initiated a period of rapid discoveries at the nanoscale. Kern et al. (1991) discovered that oxygen atoms adsorbed on a Cu(1 1 0) surface form periodic stripes of width about 10 nm. The observation has turned out to be representative of many material systems. Patterns of disks and stripes have been observed. The theory of Alerhand et al. (1988) provided the understanding of the size selection. When a submonolayer of atoms adsorb on the surface of an elastic substrate, the surface alloy often separates into two phases. The atoms at the phase boundaries have excess free energy; the phase boundary energy reduces when the phases coarsen. The difference in the surface stresses in the two phases induces an elastic field in the substrate; the elastic energy reduces when the phases refine. The phases select the size to minimize the combined phase boundary energy and elastic energy. Low energy electron microscope (LEEM) has revealed the self-assembly process in action (Plass et al., 2001). The observed thermal motion has been used to determine the forces that drive self-assembly, such as surface stress and phase boundary energy (Van Gastel et al., 2003).

The history of surface stress itself provides an example of an old idea coming of age in modern times. The surface stress of a solid, as a thermodynamic parameter different from surface energy, was pointed out by Gibbs over a century ago. Atoms on a solid surface differ from those in the interior. They have different bonding environments or may even be different species. The difference induces a residual stress in the surface of the solid. This surface stress has observable consequences in small structures. For example, molecules adsorbed on a cantilever change the surface stress and bend the cantilever. The amount of bending is measurable when the cantilever is thin. In the last decade, this phenomenon provided the basis for determining the surface stresses (Ibach, 1997). The phenomenon has also led to extremely sensitive biosensors (Fritz et al., 2000; Hagan et al., 2002).

Suo and Lu (2000) formulated a model that evolves submonolayer patterns. The model accounts for phase separation with a double-well free energy of mixing, phase coarsening with a gradient energy, and phase refining with a concentration-dependent surface stress. These ingredients constituted a phase field model, resulting in a diffusion equation with multiple driving forces. Numerical simulations reproduced patterns observed experimentally. They also showed that it is extraordinarily difficult for an isotropic system to produce perfect periodic patterns. The same difficulty has been evident in experiments. However, when orientational or spatial symmetry is broken, the system can self-assemble perfect periodic structures. Fig. 3 shows an example of the simulation.

A comparison of several assembly processes is instructive. A protein is assembled with prefabricated objects (the amino acids) using a template (the RNA). The templated assembly results in a polypeptide of a *specific*, *nonperiodic* sequence. A colloidal crystal is also assembled with prefabricated objects (the identical particles), but without a template. The lack of a template results in a polycrystal with no spatial specificity. In assem-

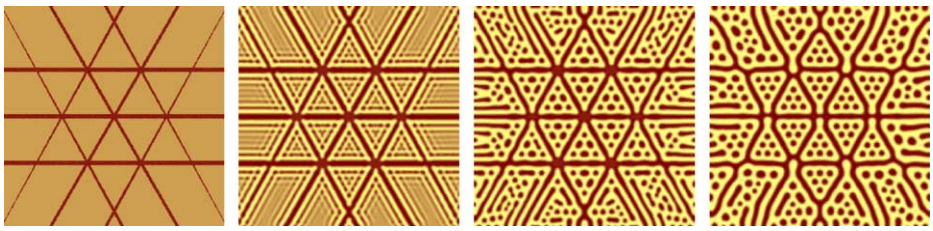

Fig. 3. A time sequence initiated with a coarse pattern of concentration field. The subsequent concentration field is affected by both the initial coarse pattern and the self-assembly force (Suo and Lu, 2000).

bling quantum dots and monolayer patterns, the size of the objects (the dots, disks and stripes) and their spatial order are both formed in the process. Self-assembled quantum dots are never single sized or ordered over a long distance. A self-assembled monolayer pattern may resemble a lattice, but has abundant imperfections. To form a perfect periodic pattern, or a specific nonperiodic pattern, one must introduce a template to guide the self-assembly. It is urgent to find means to guide self-assembly.

Molecules adsorbed on a substrate surface are electric dipoles. At an elevated temperature, one may bring a charged conducting tip to a small distance above a solid substrate. Guided by the electrostatic interaction between the dipoles and the tip, the molecules diffuse on the substrate surface, either toward the spot below the tip, or away from it (Whitman et al., 1991). The resulting molecular pattern, once frozen, leaves an electrostatic field in the space after the tip is removed. This pattern may serve as a memory device, which can be read by sensing the electrostatic field. Similarly, one may place above the molecules a mask, which is pre-patterned with a topographic surface. The electrostatic interaction transfers the pattern on the mask to a molecular pattern on the substrate. Gao and Suo (2003) have simulated this principle of guided self-assembly of submonolayer patterns. The electrodes can also be patterned and addressed at a coarse scale. After an island pattern has formed, upon reheating subject to a new voltage pattern, a different island pattern can form. The process thus offers programmable self-assembly.

1.5. The molecular car

As will be discussed, an open question for fluidics is how small they can be. This question can be addressed from a different angle. Often, what need to be moved are target molecules, not ambient liquids. One may envision a new technology, *the molecular car*, that will shuttle target molecules like passengers, with or without surrounding liquids (Suo and Hong, 2004).

Fig. 4 illustrates the concept. Consider a short-chain molecule with three characteristics: its one end adsorbs to a solid surface, its mid-chain has a group with an electric dipole moment normal to the solid surface, and its other end is a passenger receptor. The molecule has a *modular* architecture. The division of labor offers the flexibility to design separate modules, at the molecular level, to fulfill distinct functions. On the solid surface, a collection of such molecules aggregates into a monolayer island by the van der Waals interaction between the chains. Under no external force, the island undergoes Brownian motion.

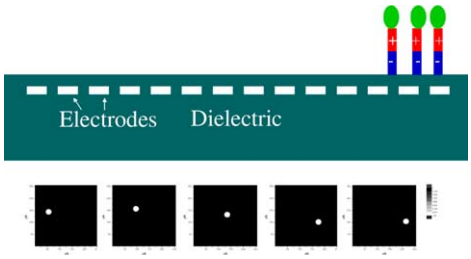

Fig. 4. The molecular car and its on-chip infrastructure (Suo and Hong, 2004).

The monolayer island is a molecular car. Fig. 4 shows an implementation of its *on-chip infrastructure*. An array of individually addressable electrode pixels is buried beneath the surface of a dielectric substrate. The monolayer island adsorbs on the dielectric surface. Unlike a bulk liquid, the molecules in the island have their dipoles aligned in the same direction. Charge the electrodes sequentially, and the resulting moving electric field propels the car to move. Because the electric field pattern is programmable, and the inertia effect of the car is damped, the car can move forward, move backward, make a sharp turn, and park. The bottom panel in Fig. 4 shows a simulated time sequence, where a single island is programmed to move on a sinusoidal path.

More generally, the car can be a monolayer island, a largish molecule, or a polymer. The surface of the chip can be patterned with immobile molecular monolayers to enhance the mobility of the car, or confine its Brownian motion. The space above the car can be a vacuum, a dielectric liquid, or a solid overpass. The car receives a passenger molecule in one pool, moves on the highway on

the chip, and then releases the passenger molecule in another pool.

The molecular car can be made *reconfigurable*. If the car is a monolayer island of weakly bonded molecules, the car can split into smaller cars in response to an electrostatic force, and the cars then move in separate ways. Conversely, several cars can merge into a single larger car, and allow passengers to mix. Implications for combinatorial chemistry for drug discovery and energy research are considerable. If the car is a largish molecule or a polymer, it can change conformation in response to light, electric field, or temperature.

In initiating any scientific and engineering endeavor, one may ask, why now? Societal needs aside, be they better drugs or cleaner energy, the answer has to do with the confluence of new tools and new knowledge. For more than a decade, experience has accumulated in using an electric field to propel microfluidics, and induce nanoscale patterns. Even more closely related to the molecular car is electric field-directed molecular migration in a lipid bilayer supported on a solid substrate (Groves and Boxer, 2002), in a lipid monolayer on air/water interface (Lee et al., 1994), and on a solid surface (Whitman et al., 1991). The invention of scanning probes has led to unprecedented control and observation of molecular motion on solid surfaces (Rosei et al., 2003). Specifically, the migration rate has been measured for many molecules on solids (Barth, 2000). Synthesis techniques now exist to knit bioreceptors and other functional groups to a single molecule. Micro- and nanofabrication can make intricate structures with ever smaller features. The development of the molecular car and its on-chip infrastructure will benefit from, and ultimately challenge, all these tools and knowledge.

The concept of the molecular car raises many questions. How do we make the car? What will it be good for? How do we search for the right molecule–substrate pair, so that the molecule migrates rapidly on, but does not evaporate from, the solid surface? Or perhaps we like an amphibian, but how do we control it? How do we measure the electric dipole moment of a single molecule adsorbed on a solid surface? Does the electrode really have the authority to direct the car to move, despite the thermal fluctuation? (How do we drive the car in a perpetual earthquake?) What will happen when two cars bump into each other? How do we load and unload passenger molecules? Do we need a global positioning system to monitor all cars on a chip? These questions may disturb the skeptic and distract the enthusiast. It is time to work out key scientific problems.

1.6. Microfluidics, nanofluidics, and nanotribology

For many engineering applications, the paradigm is *not* a mechanical device isolated from its environment. The function of having ambient fluids may be:

- To prolong lifetime (lubrication), as in hard discs, which comprise the largest single current commercial market for nanomechanical devices.
- To be the necessary matrix for interactions, as in the molecular motors of biology.
- To be the conduit for the technology, as in MEMS. It is true that MEMS channels do not yet commonly approach the nanometer level, but this is an obvious direction for the future.
- In addition, there are reasons to believe that paradigms that are taken for granted regarding bulk flow can break down when dimensions become small enough, for example regarding the classical 'stick' boundary condition. In other words, some qualitatively new features emerge when mechanical structures become sufficiently thin.

A first aspect of nanofluidics is what happens when the liquid film thickness is comparable to the size of the molecules themselves. Examples are zeolites, porous media, hard disc lubrication, and idealized geometries such as are found in the surface forces apparatus. In all of these examples it has been demonstrated that the mechanical properties of the fluid cannot be understood by extrapolating known properties of the bulk fluids (Granick, 1991; Bhushan et al., 1995; Granick, 1999). But too much of current understanding is phenomenological; for example, the hard disc industry quantifies what it calls the 'limiting shear

strength' of the fluid. However, since the mechanisms that determine such a strength are unknown, its magnitude cannot be varied rationally. What is clear is that conventional continuum ideas of fluid flow do not apply. There are intriguing parallels to the flow of granular materials—another type of system where objects lose free volume and degrees of freedom, and flow is dominated by geometrical interactions between objects of definite size and shape.

Anomalies also occur when liquid films are so thick as to be macroscopic, such that neither the viscosity of the fluid nor the dynamics of molecules within the fluid are perturbed from the bulk fluid; then the boundary conditions of how momentum is transferred during flow are found to be more problematical than has been appreciated in the past. Recent research shows that the boundary condition can vary from 'stick' (as in textbooks) to 'slip' (which saves energy) in response to physical chemical properties of the surfaces that can be controlled (Pit et al., 2000; Craig et al., 2001; Zhu and Granick, 2001, 2002; Tretheway and Meinhart, 2002; Granick et al., 2003). Fig. 5 illustrates the boundary conditions. The magnitude of this effect is measured not in a few percent, but in up to 2–3 orders of magnitude. Those studies have mostly been performed to date only in idealized situations, however. It is not yet known definitively how they will scale up to fluid channels. Some aspects of the mechanisms are understood, for example the surprising fact that the degree of 'slip' correlates with the chemical makeup of gases dissolved in the fluid. Other aspects are not understood, for example the correlation with the presence of surfactant within the fluid, and with the presence of fluffy polymer chains at the surface. These issues have been reviewed (Granick et al., 2003).

It is fair to ask why these anomalies were not recognized until recently, as the underlying ideas are not new. The main point is the advent of new technological capability. Unless solid surfaces are sufficiently smooth, roughness itself will create the conventional stick boundary condition. Even if solid surfaces are smooth, the 'slip length' does not exceed some micrometers or tens of micrometers, and is too small to perturb fluid flow of channels that are substantially thicker than this. This having been said, there are suggestions that the Lotus Leaf effect (Onda et al., 1996) can produce 'slip' even in thicker channels (Watanabe et al., 1999); the mechanism is presumably that super-rough surfaces trap so much air between the surface and the fluid that when fluid flows, it passes primarily past nothing but air itself.

Of special importance for nanofluidics is water. Common experience shows that when water meets a hydrophobic surface it beads up. This commonplace observation and theories that it has stimulated (Lum et al., 1999) have been enriched by recent experiments showing that in idealized

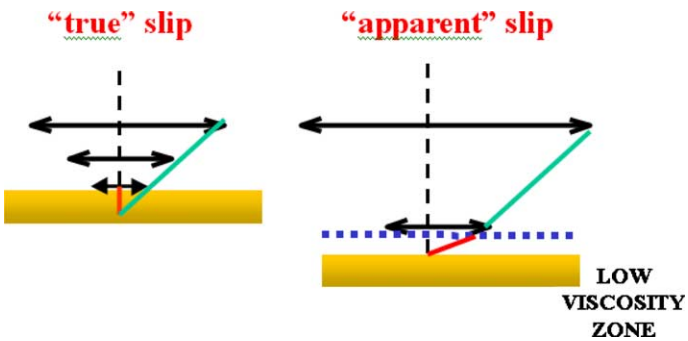

Fig. 5. Schematic illustration of the distinction between true slip (left) and apparent slip (right) in oscillatory flow. In both cases the velocity of the moving fluid extrapolates to zero at a notional distance inside the wall and is finite where it crosses the wall, but the physical reason is fundamentally different. For true slip, it is literally so. But it may also happen that a low viscosity component in the fluid facilitates flow because it segregates near the surface. It appears that the presence of a low-viscosity zone can be engineered deliberately, even by subtle methods of gases dissolved in the moving fluid (Granick et al., 2003).

situations involving hydrophobicity imparted by rather perfect self-assembled organic monolayers terminated with methyl groups, the water appears to dewet the solid. "Nanobubbles" (Tyrrell and Attard, 2002) or perhaps a nanometer-thick vapor gap separate the solid (Zhang et al., 2002) from the dewetted fluid; these and other experiments have been reviewed (Ball, 2003). There are obvious fundamental scientific issues involved. From the point of view of fluidics, this can help to explain breakdown of the classically-expected 'stick' boundary condition of fluid flow. Not yet understood is how this may depend on perfection of the hydrophobic surfaces, nor how it may depend on the presence of polar impurities. Solid surfaces comprised of a mix of hydrophobic and hydrophilic patches may produce interesting patterns of fluid flow. We emphasize that self-assembled structures are often exquisitely sensitive to external fields that may be present during their formation, of which the most common are the electric and magnetic fields and the shear flow of fluids in which the building blocks are suspended. Still unclear at the conceptual level is whether these field-sensitive structures are some kind of nonequilibrium most-stable structures, or states of minimum energy dissipation.

1.7. Some other issues related to nanofluidics

How does mechanics change when nanometer-sized structures are involved? Fluid mechanics in small systems is at an early stage of understanding. It is evident already, as discussed in more detail above, that the viscosity of even the simplest fluids can be altered in the immediate vicinity of a solid boundary, and this has obvious importance for making rational advances in the emerging fields of nano- and microfluidics. But existing work is limited by aspects specifically related to the insufficient development of self-assembly, for example:

- Poor understanding of the self-ordering tendencies of fluids at solid surfaces.
- Poor capacity to intentionally produce solid surfaces of controlled functionality. The best progress has been accomplished in making homogeneous surfaces. To produce patterned patchiness (chemical as well as topographical) where the order is long-range but the building blocks are nanometer- or micrometer-sized is in the realm of dreams.
- An area of great opportunity is to address squarely the fact of life, that many of the most interesting and relevant systems for nano- and microfluidic flow are not Newtonian (as has been assumed almost universally) but viscoelastic. Examples include the microfluidic manipulation of cells, of surfactant microstructures, and of proteins whose concentration is not dilute. This important class of problems is almost untouched.

The integration of mechanical experiments with other local probes—focused X-ray beams to measure structure, and other methods to measure dynamics—holds special promise. Among these, principles of fluorescence spectroscopy constitute a sensitive and discriminating approach to measure the local nanoenvironment that underlies an overall mechanical response. For example, sliding friction when molecularly-thin liquid films separate two solids is of tremendous practical significance in the field of mechanics, but progress in understanding it has been impeded by the paucity of methods capable of its investigation at the molecular level.

Recent work has augmented sliding friction studies by in situ measurement of self-diffusion, using fluorescence correlation spectroscopy of the mobility of individual dye molecules. The mobility of fluorescent molecules embedded within molecularly-thin films at nanomolar concentrations reflects mobility of the local nanoenvironment. Spatially-resolved measurements within a Hertzian contact after passing from rest to kinetic sliding showed that translational diffusion depends only weakly on the shear rate, contradicting past mechanical measurements that suggested significant dynamical (and even structural) changes of such films. Intriguingly, the films became significantly more homogeneous during sliding, in the sense that diffusion processes become less polydisperse. The oft-hypothesized shear-melting hypothesis of sliding friction was not confirmed at the molecular level (Mukhopadyay et al., 2002; Mukhopadyay and Granick, submitted).

1.8. Time is right for a mechanistic approach to self-assembly

This is a time when many new tools have reached a high level of sophistication, but have been insufficiently applied to these problems of mechanics. For example, it is conceivable to catch self-assembly in action by exploiting the X-ray intensity and ability to record data with sufficient speed to follow assembly processes in real time in advanced synchrotron sources. However, the community of scientists knowledgeable about the synchrotron is insufficiently aware of the basic problems of self-assembly. Similar limitations characterize the use of other imaging tools (e.g., confocal and scanning probe microscopes), modeling tools (e.g., statistical mechanics and parallel computing), and patterning techniques (e.g., nanoimprint and extreme ultraviolet lithography).

Many issues that have emerged from the above discussion are central to self-assembly: the need for mathematical optimization techniques applied to complex systems; resolution of the prevailing confusion regarding the vital issue of which self-assembled structures are equilibrated, which are metastable, and which are simply arrested in some glassy state along a kinetic pathway; mechanochemistry (e.g., chemistry and mechanics at interfaces); and reliable methods to guide direct self-assembly. The mechanistic approach is paramount in all of these instances to achieve resolution. Only if the mechanistic approach takes the natural leadership role will revolutionary advances be made in this field. The field is wide open, from basic understanding to system integration.

2. Section 2: mechanics in biological, bioinspired, and hybrid material systems [4]

2.1. Introduction

A key focus of many workshop presentations was the role of mechanics in defining new directions in biological and bioinspired material systems. Mechanics plays a fundamental role in understanding the biological functions at all scales. We are just beginning to utilize biology and biological techniques to develop new materials and devices that will have broad impacts on engineering. For example, we must strive to learn the mechanism of energy transduction at the biomolecular level and begin to apply it and improve on it for new engineering systems. We need to investigate the hierarchical nano- and microstructure of biological materials (e.g., nacre, bone, wood) and develop new multiscale-designed materials that adopt the deformation and fracturing modes of the biological systems. A cautionary note as we explore this area is that, in engineering applications, both robustness and efficiency are necessary, whereas in biology robustness alone is sufficient. We can become more efficient in designing material systems by borrowing from and learning from biology, but we must exercise caution.

The time is ripe for exploration in this rich area because new experimental and simulation tools are now available to study confined liquids, liquid–solid interfaces, nanostructures, and biomolecules at interfaces. In addition, now there is a great deal of interest in understanding and exploiting molecular biology for applications in materials science and engineering, requiring a unique interdisciplinary partnership that is creating a new group of researchers with knowledge in multiple fields. This presents an opportunity for new discoveries and most likely may lead to significant progress in both science and technology.

Below we first list the unique features of biological and bioinspired materials. These then lead into some of the research examples that were presented in the Workshop. Key open scientific questions are explained and then future directions for research are highlighted. Mechanics researchers will have key contributions to all of the areas listed below. Mechanics must play a leadership role in the development of hierarchically designed bioinspired materials. In addition, mechanics must lead the effort of awakening biologists to the importance of forces and motion that are invariably coupled to the more familiar biochemical processes in biological systems.

[4] Prepared by G. Bao, L. C. Brinson (coordinator), H. Gao, L. Mahadevan, A. Majumdar, S. Nemat-Nasser.

2.2. Unique features

In biological materials, structure and function are integrated at all scales, starting from submicron features. The understanding of these features and their relations to the material's overall response and motion is fundamentally critical in developing new bioinspired and hybrid material systems. Below is a partial list of some of these unique features that have been examined at the Workshop, and which are believed to be instrumental in identifying the key questions and future research directions.

- *Size scale*. Features and microstructure at 1 nm–100 μm provide a rich interplay between competing forces. Examples are:
  - Protein dynamics during folding and motor movements (1–10 nm).
  - DNA sequencing and separation devices using nanomechanical probes (10 nm+).
  - Cytoskeletal polymers that involve a variety of persistence lengths, and crosslinkers which give rise to passive/active ordered/disordered structures (100 nm+).
  - Nanotubes used as probes, sensors, and actuators (1 nm+)
    - AFM tips;
    - biosensors and actuators;
    - electrical sensors and actuators;
    - stress-induced reactions.
  - Hierarchically designed structures (1 nm to 1 mm)
    - Structurally reinforcing networks;
    - biological systems (abalone, nacre, bone, teeth...).
- *Time scale*. Events that occur in time scales from picoseconds to seconds. Examples are:
  - Fracture of biomaterials: individual bond breaking in picoseconds.
  - Turnover time of carbonic anhydrase enzyme in microseconds.
  - Protein conformation changes occur on microsecond + time scale.
- Geometry and topology are extremely important at nano- to microlength scales because surfaces dominate volumes. Examples of some resulting effects are:
  - Inextensibility
    - Linear polymers are easier to bend than extend;
    - cell membranes are easily bent and sheared, but are nearly inextensible.
  - Impenetrability
    - Entanglement;
    - packing problems in molecular biology: cm long DNA packed into 1 μm nucleus.
  - Confinement
    - soft materials in confined spaces dramatically change properties (e.g., abalone shell, nacre);
    - nanofluidics in confined spaces (e.g., hard to mix, influence of hydrophobicity on no-slip conditions).
- Thermal fluctuations play an important role in soft materials/biological systems. Unlike in hard materials where $E_{\text{hard}} > kT$, in soft materials $E_{\text{soft}} \approx kT$. Hence, both continuum and statistical mechanics complement each other in characterizing these systems.
- Phenomena are characterized by interplay between chemistry (conformation, binding/reaction), physical chemistry (hydration/solvation, electrostatic, van der Waals) and mechanics (force/motion/deformation).

2.3. Nanomechanics at the interface of soft and hard matter

Mechanical forces generated during biomolecular binding. Recent experiments have shown that specific biomolecular binding on one surface of a sufficiently compliant mechanical structure produces mechanical forces that deform the structure (Thundat et al., 1997; Raiteri et al., 1999; Fritz et al., 2000; Wu et al., 2001a,b). For example, a reaction on one surface of a microcantilever beam bends the cantilever (Fig. 6), since all specific biomolecular interactions result from the reduction of free energy. Hence, when the free energy of one cantilever surface is reduced, the resulting lowering of the surface free energy density (surface tension) creates a bending moment that bends the cantilever. Because free energy reduction is the common driving force for all reactions, this mechanical ap-

proach has become a common platform for detecting a variety of biomolecular binding such as DNA hybridization, protein–protein interactions, DNA–protein binding, and protein–ligand binding. This has major implications in biotechnology and is leading towards a universal platform for studying biomolecular assays in a high-throughput manner. Nevertheless, the origins of mechanical forces are not well understood. While the thermodynamic argument provides a global explanation, it is bereft of detailed mechanisms. The four interaction forces that would prefer larger bending are: direct electrostatic repulsion; osmotic pressure; configurational entropy of the biopolymers; and hydration/solvation forces. The force that opposes larger bending is the elastic strain energy of the cantilever. Theoretical work (Hagan et al., 2002) suggests that electrostatic and configurational entropic forces are negligible for molecules such as DNA. However, it has so far been difficult to isolate the contributions of osmotic and hydration forces, although experiments using a microarray chip are currently underway to further dissect the problem (Majumdar and coworkers).

Fluid mechanics in nanotubes. When a glass surface is exposed to water, its surface becomes negatively charged due to the release of protons from the surface OH bonds. In an ionic solution, this leads to an electric double layer characterized by the Debye length, within which positive ions are attracted and the negative ions are repelled. The Debye length is typically in the range of 1–50 nm, depending on the bulk ion concentration. It is now possible to fabricate (Fan et al., 2003) glass nanotubes with internal diameters in the 10–30 nm range. In some cases, it is smaller than the Debye length. Calculations by Majumdar and coworkers and their experiments suggest that when the bulk ion concentration is sufficiently low, the region inside these tubes contains only positive ions, in order to balance the negative ones on the glass surface. Hence, it is possible to produce unipolar solutions. Such a device provokes many questions: what happens if a pressure-driven flow is superimposed on it? What happens to the electrophoretic and electro-osmotic flow if a voltage bias is applied across it? These have remained unanswered. Majumdar and coworkers are in the process of exploring this area by making a unipolar ionic field-effect transistor, where a gate electrode controls the surface charge and thereby modulates the ionic current through the nanotube (Fig. 7).

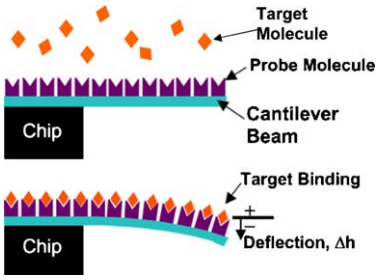

Fig. 6. Generation of motion in mechanical devices such as cantilevers due to specific biomolecular reactions between DNA, proteins, and other chemicals (Wu et al., 2001a).

2.4. Transport of DNA and polypeptides through carbon nanotubes

Gao et al. (2003) have used atomistic simulations and statistical mechanics to study the encapsulation of DNA molecules inside carbon nanotubes (CNT); see Fig. 8. In recent years, bionanomaterials science has emerged as a new exciting field in which theoretical and experimental studies of structure, function and behaviors of DNA, RNA and protein together with nanostructured metal, ceramics, glass, and semiconducting materials have become a focus. The interdisciplinary area between materials science and biology is a very fertile field of research where one can not only search basic principles of materials synthesis and design in the biological world but also apply the basic principles of mechanics and physics to model bionanomaterials systems. This study involves encapsulating DNA and peptides inside CNT for potential applications in molecular electronics, molecular sensors, electronic gene sequencing and gene delivery systems. MD simulations based on a molecular force field allow us to find the effects of CNT radius, CNT end-group, multiwalled vs. single-walled CNT, double- vs. single-stranded DNA and temperature on the dynamics of the DNA encapsulation process. Statistical mechanics methods are used to model and confirm

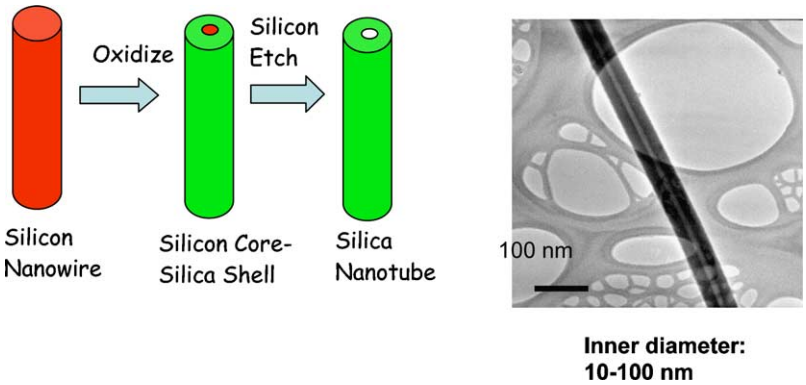

Fig. 7. Fluid and unipolar ion transport in silica nanotubes and results from a nanofluidic transistor—possibility of electrochemo-mechanical energy conversion, ion separation (Fan et al., 2003).

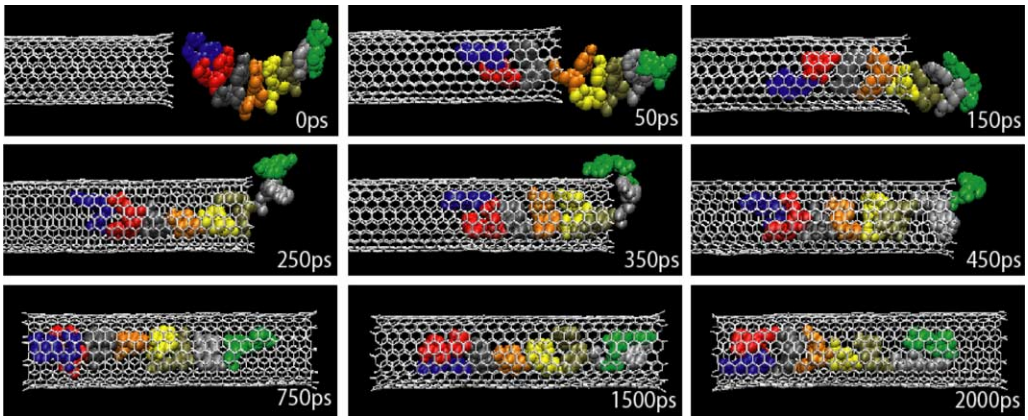

Fig. 8. Simulation snapshots of oligonucleotide interacting with (10, 10) CNT in water after 0, 50, 150, 250, 350, 450, 750, 1500 and 2000 ps. Water molecules are not displayed for clarity (Gao et al., 2003).

MD simulations of a flexible polymer chain being encapsulated in cylindrical confinement.

In another study, Daiguji et al. (in press) have used mechanics at the atomic and statistical level to propose molecular assembly of nanotubes as liquid-state ionic transistors, which in combination with biomolecules, has the great potential of achieving nanoscale manipulation and transport of biomolecules; see Fig. 9.

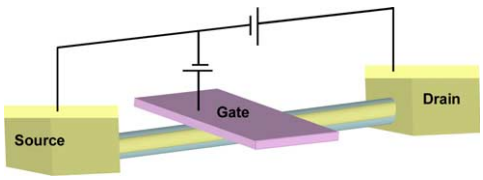

Fig. 9. Molecular assembly of nanotubes as liquid-state ionic transistors (Daiguji et al., in press).

2.5. Mechanistic view of structure–properties relation and robustness in nanostructured biomaterials

Active and passive mechanics of cytoskeletal assemblies. The mesoscale mechanics of ordered and disordered networks/assemblies offers unique opportunities for material design using the exquisite control that molecular biology allows. For example, by using actin and microtubule binding proteins we can construct networks with a range of rheologies with moduli that vary over 3 orders

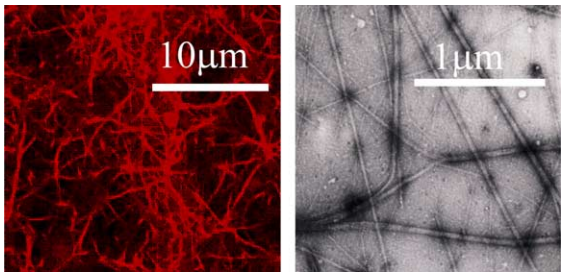

Fig. 10. Highly crosslinked microstructures result from actin and tight crosslinker scruin.

of magnitude in the linear and nonlinear regime (Fig. 10). Motor proteins can be used to construct networks that are dynamic, i.e, with dynamic rheologies that can allow us to biomimic the locomotion of cells and thus open new avenues in bioMEMS. Similarly, ordered assemblies of cytoskeletal proteins such as actin and microtubule crystals are known to have different symmetries and transitions that are similar to martensitic transformations in inorganic materials. Finally, polarized growth can also lead to motion and indeed is the basis of cell motion which arises from sol–gel transitions. These systems not only throw up new theoretical questions that are relevant for mechanics, but suggest the harnessing of these ideas to self-assembled structures inspired by biology (Balaeff et al., 1999; Mahadevan and Matsudaira, 2000; Shin et al., 2003; Cohen and Mahadevan, 2003).

Selection of nanoscale size for flaw insensitive design. Robustness and fitness are the key to survival in biological systems. Therefore, biological materials, especially those designed to sustain mechanical loads such as the endo- and exo-skeleton systems including abalone shells, teeth and bones, are designed mainly for robustness. These materials are nanocomposites of hard mineral crystals embedded in a soft protein matrix. While the mineral phase provides the necessary stiffness and hardness, the protein matrix provides a multitude of relaxation functions which greatly enhances the toughness of biomaterials, up to three orders of magnitude in fracture energy in comparison with the pure mineral phase. Mechanics has played a leading role in a recent study by Gao et al. (2003), which shows that the nanostructure, in particular, the nanometer size of mineral crystals, is selected to achieve maximum tolerance of crack-like flaws (representing protein remnants) inside the biomineral phase. A similar study of the strength of biomaterials under compression reveals that the slender mineral particles resist buckling also in a mechanically robust way: The buckling strength becomes insensitive to geometrical variations due to protein support and confinement. Further investigations of hierachical structural design based on mechanics principles may provide design guidelines for development of hierarchical nanostructured materials.

Design of hierarchically nanostructured materials such as nanotube reinforced composites. Inspired by the hierarchical design of biomaterials (Figs. 10 and 11) and the capability for improved material properties of simultaneous stiffness, strength and toughness, nanostructured polymeric composites are ripe for exploration. In these systems, the exposed surface area of the nanoparticles is orders

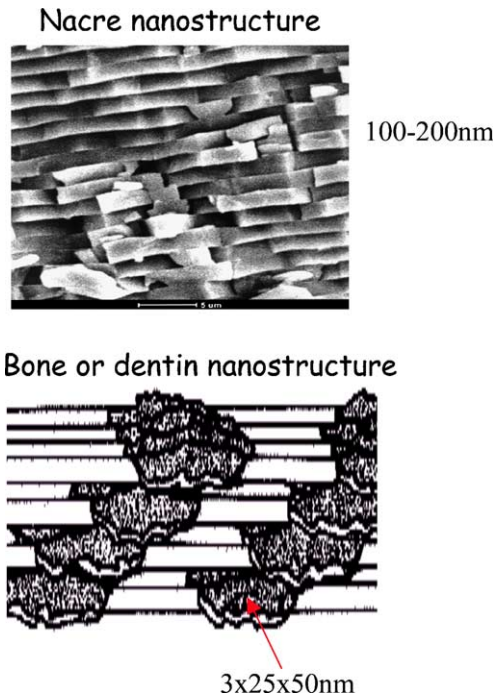

Fig. 11. Biomaterials exhibit complex hierarchical composite structures (Gao et al., 2003).

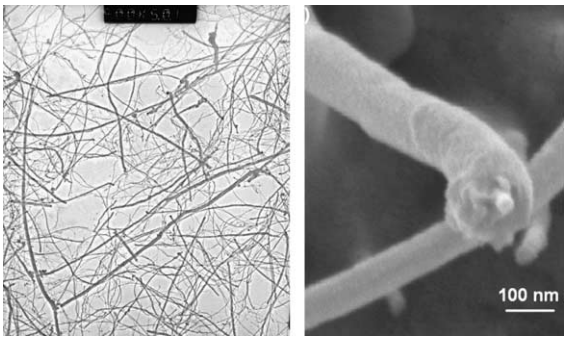

Fig. 12. Electron microscopy images of polycarbonate—multiwall nanatube composite: left showing entwined nanotube networks and right showing polymer sheath on nanotube protruding from fracture surface, indicative of extensive reduced mobility interphase layer (Fisher et al., in press; Ding et al., in press).

of magnitude over that of traditional polymer composite systems. Hence the interplay between the chemistry of the nanoreinforcement and the polymer and the morphology of the network provide a limitless domain for optimization of enhanced material properties. It has already been shown that an extended polymeric interphase region exists with dramatically changed mechanical properties even in systems with less than 2% nanotube reinforcement. Wide open areas to understand include defining the nature of the interphase zone and its role in the deformation and failure of these systems (Fig. 12). Experiments, modeling and simulation from the nano to the macroscale are needed to advance this area. For references, see Fisher et al. (2003), and Schadler et al. (2003).

2.6. Surface effects

Surface force apparatus combined by femtosecond optical excitation can be used to study dynamics of ultrathin liquid films such as examining the no-slip condition. Anomalies occur when liquid films are so thick as to be macroscopic, such that neither the viscosity of the fluid nor the dynamics of molecules within the fluid are perturbed from the bulk fluid; then the boundary conditions of how momentum is transferred during flow are found to be more problematical than has been appreciated in the past. Recent research shows that the boundary conditions can vary from 'stick' (as in textbooks) to 'slip' (which saves energy) in response to physical chemical properties of the surfaces that can be controlled; see also, comments in Section 1.6. The magnitude of this effect is measured not in a few percent, but in up to 2–3 orders of magnitude. Those studies have mostly been performed to date only in idealized situations, however. It is not yet known definitively how they will scale up to fluid channels. Some aspects of the mechanisms are understood, for example the surprising fact that the degree of 'slip' correlates with the chemical makeup of gases dissolved in the fluid. Other aspects are not understood, for example the correlation with the presence of surfactant within the fluid, and with the presence of fluffy polymer chains at the surface. These issues have been reviewed by Pit et al. (2000), Craig et al. (2001), Zhu and Granick (2001, 2002), and Tretheway and Meinhart (2002).

Surface roughness can be controlled to produce super-hydrophobic (SH) surfaces. The roughness leads to very small contact areas where the liquid actually meets the substrate, a phenomenon known as the Lotus effect. The final result is that on a substrate with appropriate roughness a liquid will appear as a near perfect sphere, ready to roll! SH coatings can be made by lithography as well as via self-assembly routes, and have much promise for low-friction microfluidic devices.

2.7. Open scientific questions

- How is free energy transduced to generate motion (both unidirectional and cyclic) from chemical reactions—mechanochemistry?
- How can one relate structure to function via mechanics in biomacromolecular assemblies?
- How do you switch from solid-like to liquid-like behavior in cytoskeletal networks (sol–gel transition) in the context of cell motion?
- How do you design a hierarchical structure to optimize specific properties?
- What is the nature of liquids in close proximity to a solid surface, especially water in proximity to hydrophilic and hydrophobic surfaces? There is a disconnect between real (chemical/physical roughness and heterogeneity) and ide-

alized surfaces. How do molecules and ions diffuse and transport in confined liquids under external thermodynamic potentials? Can liquids and/or macromolecules be used for generating mechanics in solids—phase transitions, plasticity, etc?

2.8. Future directions

- How to link from atomistic to micromechanisms in basic deformation modes and failure in nanostructured or biomaterials?
- How to combine atomistic, statistical and continuum approaches? For example, understanding protein folding and mis-folding; rheology of disordered networks. These problems involve coupling between multiple length and time scales.
- Development of new experimental techniques to accurately probe dynamical evolution of bionanomaterial response
  - improvement in temporal and spatial resolution (protein machine);
  - to discriminate single versus ensemble molecular events at surfaces/interfaces.
- Interconnection between experiment and theory/simulation is crucial to answering the open questions in nanobiomaterials.
- Nanomechanics at the interface between liquids and solids with biomolecules is critical for materials and mechanics research, especially for new biomaterials synthesis, friction and dissipation, and energy conversion.
- Possibility of fabrication and replication of nanostructures, e.g., using self-assembly.

3. Section 3: inelasticity and fracture [5]

3.1. Introduction

Inelastic material behavior, especially when coupled with fracture, represent a long-standing problem area within the realm of solid mechanics. However, many key aspects have surfaced and new challenging issues have emerged with the development of nanomaterials, MEMS/NEMS and biopolymers. Old problems, e.g., fragmentation and shear instabilities, need to be revisited from a different and multidisciplinary perspective, taking advantage of more powerful computers and new experimental tools. In addition, there are problems which were previously ignored or left untreated because the length and time scales of interest were not considered essential. Now, however, with the rise of importance of nanoscale structures with high surface to volume ratios, many of these unresolved topics require a fundamental mechanistic understanding. There are truly new areas of mechanics, specifically in plasticity, viscoelasticity and fracture, that require an infusion of multiscale experimentation and modeling. Examples are the behavior of integrated materials systems (e.g., soft plus hard materials in an artificial or man-made structure), and predictive material modeling of micro/nanostructural features for specific properties and nanostructures.

Recent innovations in recovery experiments have allowed direct characterization of thermomechanical response of many metals over a broad range of strain rates and temperatures. It is now possible to construct isothermal stress–strain relations for metals of high yield stress at high strain rates and at various temperatures from liquid nitrogen to 1000 °C and greater; see Nemat-Nasser and Issacs (1997, 1998, 1991), and ASM Handbook (2000). With these tools, it is possible to measure directly the plastic workhardening at various (constant) temperatures and (constant) strain rates, for strains exceeding 100%, and hence separate the workhardening from strain-rate and temperature effects. Within deformation regimes where plastic deformation occurs by the motion of dislocations, these experimental tools can be used to separately measure the athermal, the thermally activated, and the drag-induced resistance to the motion of dislocations. This approach naturally involves length-scales that directly relate to the dislocations and the associated microstructure.

Composite, multiphase, functionally-graded, and artificially structured materials are of enor-

[5] Prepared by C. Barbour, H. Espinosa (coordinator), P. Gumbsch, H. Gao, K-S. Kim,.W. Knauss, L. Kubin, and B. Larsson.

mous and increasing technological importance. They represent areas in which a fundamental understanding of mechanical properties derived from the constitutive interactions between interacting subsystems, their gradients, and patterned structures under stress and large deformations is needed to provide directions for optimization of the synergy between heterophases.

In this regard, an aggressive development of new experimental methods and tools is required to address mechanical, structural, chemical, and electrical phenomena encountered in micro- and nanoscale structures, surfaces, thin-films, and bulk specimens. Non-destructive, in situ probes and external multiprobe capabilities are needed in addition to sample-consuming methods. Advanced interrogation techniques allowing for detailed and direct linkage between theory and modeling are also required. Moreover, it is critical that such instrumentation investments find their way into open user facilities such as the Nanoscale Science Research Centers, synchrotron X-ray user facilities, electron microscopy centers, and nanofabrication user facilities, as well as individual university and national laboratory user facilities.

Increased efforts are needed in the design of critical research programs directly linking advanced structural and mechanical measurements. This includes detailed and well-defined modeling to provide definitive tests of any evolving understanding in terms of fundamental physical processes and processing techniques, directed toward the overall goal of the development of predictive capabilities on scales ranging from the mesoscale to the nanoscale and, ultimately, to atomic sizes.

While each of the topics listed below describes basic problems in materials behavior and fracture, and deserves a broad discussion for justification, we limit their presentation to a topical identification in the interest of brevity and conciseness:

- Predictive capabilities for many physical mechanics issues are inadequate and very limited because the continuum models are too simplistic; they typically do not, or do so in a very limited fashion, include:
  - chemistry;
  - length and time scales;
  - limited statistical/probabilistic effects;
  - insufficient loading path dependence;
  - underlying mechanisms and material micro/nanostructure specificity;
  - initial state of material micro/nanostructure;
- The gaps between modeling size scales—particularly linking continuum to discrete or atomistic to QM dimensions. These are still too large.
- Quantitative measurements at small scales. These are virtually nonexistent and need to be developed.
- Amorphous materials, e.g., polymers, metallic glasses. These need to be better understood in the context of engineering designs, and the requisite tools need to be developed.
- Degradation effects and their interaction with mechanical issues.
- Friction/fracture coupling.
- Fatigue/fracture coupling in the context of nonlinear material behavior.
- Scaling of dynamic fracture process and understanding of nonlinear material responses including friction and deformation-rate dependence.
- Fragmentation, energy absorption and dissipation for safe and blast resistant structures.
- Failure of nanoassembly systems and their possible dependence on nonlinear material response, e.g., plasticity.
- Nonlinear characterization of structural polymers in other than uniaxial tests. This is virtually nonexistent.

The more general issues that need continued attention for the evolution of a successful research program in solid mechanics are delineated.

3.2. Interaction between modeling and physical measurements

The specific issues arising out of the interaction between experiment and modeling are discussed in this paragraph. Major advances have taken place in recent years in the continuous development of cost efficient and fast computers, as well as the evolution of novel and powerful experimental tools based on electron, X-ray and probe microscopy.

Fig. 13 outlines the current perception of how that goal is to be pursued, although it does not

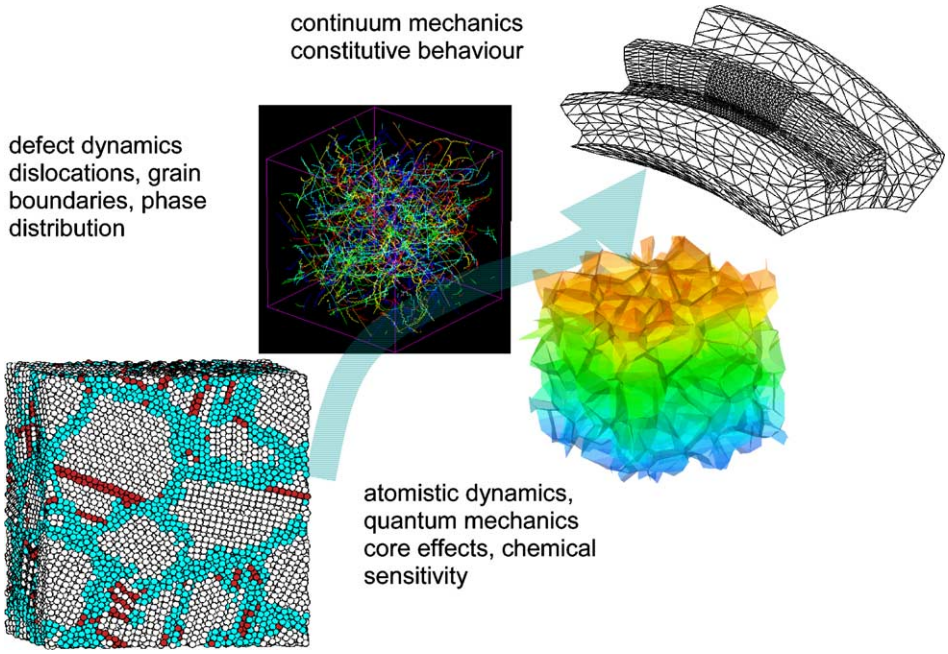

Fig. 13. Schematic of modelling at various scales ranging from atomistic to discrete dislocation and finite element modelling of components (Gumbsch, 2003).

illustrate the definitive methodology for achieving this goal.

3.3. Multiscale modeling

Mechanisms for crack nucleation. This is a subject that has received very little attention in the past, can and should now be studied computationally and experimentally. To date, there are no physically-based models available to describe crack initiation or to predict cleavage planes of a crystal. Atomistic, quantum mechanical and mesoscale modelling of crack nucleation from defects including dislocations, grain boundaries and surface steps need to be performed. It is clear that such an effort cannot proceed in a meaningful way without the clear physical identification of the formation of such defects. At issue here is the potential difference between our mental concept and the physical reality of fracture initiation processes. The formation of cracks from an apparent continuum in a fatigue environment needs to be systematically assessed. These topics are becoming increasingly important to address reliability questions in micro- and nanoscale systems and also to build multiscale models of materials strength in macro-scale applications.

Fracture. Multiple cracking, brittle to ductile transition (see more detail below), quantitative prediction of shear localization leading to fracture, and crack features including speed and path are all problems that require intensive clarification. Predicting crack propagation topology as a function of component geometry, loading condition and material microstructure remains a major challenge with respect to a wide range of materials and at any size-scale. Fig. 14 illustrates a zigzag crack pattern, which can develop in silicon single crystals. Current understanding and models are inadequate to explain this phenomenon.

Brittle-to-ductile transitions. This is another example of an important unresolved scientific issue. A fundamental understanding of this phenomenon is far from available, most assuredly because the deformation response (flow) characteristics of many materials, whether metallic,

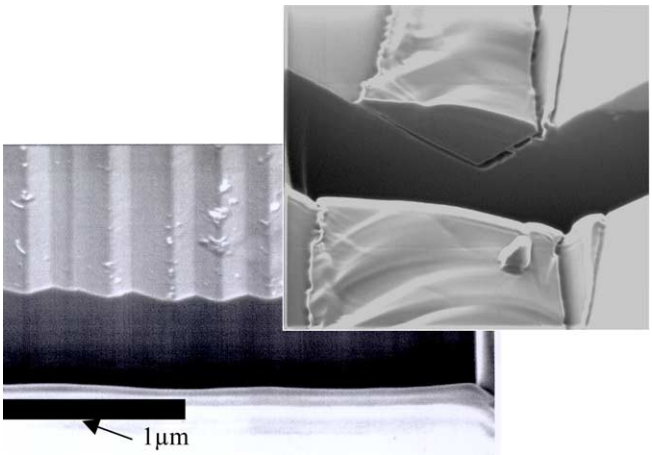

Fig. 14. Zigzag crack patterns, in contrast to planar crack, observed in silicon single crystal under certain conditions. Based on Cramer et al. (2000).

polymeric or of the ceramic type, are not sufficiently well understood as a function of temperature. In addition, the incorporation of such potential material descriptions into computational models flounders, most likely, on the simplicity with which plasticity governed behavior is incorporated into fracture descriptions (see Section 3.1). This important issue needs to be addresses from several perspectives: For example, it is important to determine to what degree the nucleation of cracks from notches or material inhomogeneities, can be understood independently of the role of microstructure on the brittle to ductile transition.

The transfer of this knowledge to component assessment is also a major goal. The details of these processes were regarded as being of little importance since their complex nonlinear interaction could not be assessed. Multiscale experimental studies and modelling can now begin to provide the framework for the investigation of these processes. However, in this area there is a particular shortage of dedicated experiments which can be used to gain physical insight and to interact with model developments in this area. The emergence of new local probing techniques, such as X-ray microdiffraction in the case of metals, can tremendously help here. It is gradually becoming realistic to confront the three-dimensional modelling of elementary processes occurring at the atomic scale. This modelling must particularly include the atomistic processes at the crack tip, like the bond breaking or slip processes, crack nucleation (e.g., at grain boundaries and notches) and dislocation nucleation. Similarly, 3D dislocation based modelling of the near tip processes, such as the evolution of the crack-tip plastic zone and of dislocation multiplication near the crack tip can now be investigated, provided the corresponding physical observations can be experimentally documented. Furthermore, incorporation of these mesoscale models into macroscopic constitutive relations, which can be used in component evaluation, is still an open, but important, issue.

Polymeric materials. In contrast to nonlinear behavior of metallic components as represented by plasticity phenomena, the understanding of the corresponding behavior in (structural) polymers is virtually nonexistent. The failure/fracture of polymeric structures is correspondingly poorly (i.e., not at all) understood. The lack of understanding the nonlinear time-dependent behavior is the bottleneck. This state of understanding is the more surprising, in that the use of polymers, by volume, in engineering equals at least that of metals. This deficiency is impacting the way industry from automotive to computer chip manufacturing can make use of polymers and apply them in systems.

3.4. Experimentation at the micro- and nanoscales

Progress in this area of mechanics is severely impacted by the lack of suitable instrumentation and methods, because

- It is difficult to manufacture reproducible small-scale specimens.
- Design and manufacturing of controllable mechanical loading fixtures for small scale specimens.
- Metrology at the atomistic and nano scales, beyond optical imaging, which is insufficient.
- New instruments such as synchrotron, analytical TEM and probe microscopy require development of in situ specialized tools in open user facilities.
- High resolution local methods for measurement and characterization involving high temporal resolution.

There is a strong need for the development of novel methods adapted to in situ electron and probe microscopy. Current capabilities in this regard are limited in many respects. For instance, load and deformation histories are not measured independently nor in real time. Although techniques for deformation imaging at the atomic scale are emerging, they are typically based on transmission electron microscopy (TEM) and ultra-high vacuum scanning tunneling microscopy, which is only applicable to conductive materials. Both present significant challenges that will need to be overcome for true atomic characterization. For example, CCD cameras available in the characterization of dislocation motion in in situ TEM investigations, are not fast enough to capture discrete nucleation and propagation events. Moreover, deformation measurements with these tools are today understood to mean image progression. By contrast, the direct determination of strains (fields of strain) requires a much higher precision of these tools that have not been addressed at all, neither in the mechanics community, nor in the probe manufacturing area.

The integration of specimens to microdevices is another aspect that requires particular attention. In this respect, tools for nanomanipulation with feedback control as well as appropriate gripping strategies are required. Only limited progress is

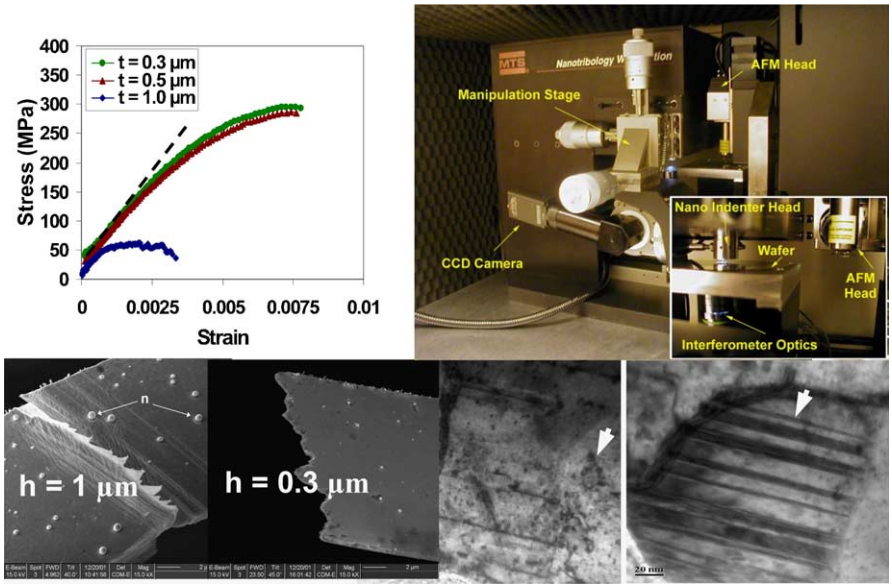

Fig. 15. Plasticity size scale effects in submicron freestanding fcc thin films under pure tension identified by a new membrane deflection experiment (Espinosa et al., 2003, in press).

being made in this area (Fig. 15) and much remains to be accomplished. Thus, it is essential to develop tools and instrumentation appropriate for measurements at the needed size and time scales to perform critical experiments supporting the understanding of phenomena at the submicron level, as opposed to those governing macroscopic situations or processes. Requisite equipment, roughly paralleling macroscopic engineering facilities, do not exist. A serious effort to develop such instrumentation allowing, specimen manufacture, gripping, and force deformation field analysis, needs to be developed so that supporting analyses can be executed. Fig. 16 illustrates the usage of an integrated AFM-Nanoindenter in the identification of size scale plasticity effects in freestanding fcc films.

New microfocusing and coherent diffraction synchrotron X-ray techniques have been developed for 3D investigation of the local structure and strain in crystalline materials. High energy applications penetrating to depths of mm's to cm's achieve resolution on the order of 5 μm (Poulsen, 2002, 2003) while medium-level energy techniques have demonstrated submicron resolution over 10–100 μm, (Larson et al., 2002; Yang et al., 2003). Coherent diffraction imaging techniques are beginning to probe the nanoscale, (Miao et al., 2002; Robinson et al., 2001). These capabilities are new and developing rapidly so that increased resolution can be expected over the next few years. Spatially resolved, three-dimensional determinations of crystal lattice rotation and stress can be performed in both post-mortem and in real time, (i.e., under stress) with these new techniques. Such nondestructive information appears to provide a key for the interpretation of experiments and to integrate experiment and modeling capabilities on length scales ranging from the continuum to the nanoscale. This is illustrated in Fig. 16.

A distinct need exists for clean/reproducible samples with uniform microstructure in order to perform mechanical measurements. These

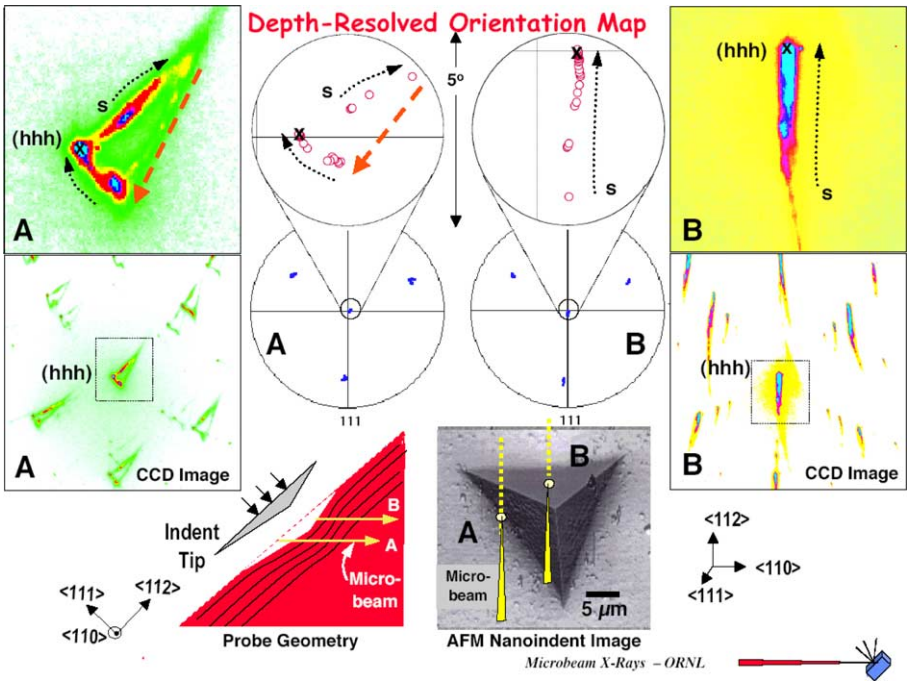

Fig. 16. Illustration of coherent diffraction synchrotron X-ray characterization of crystal lattice rotation and stress under a nanoindented region.

types of samples are essential to elucidate mechanisms of deformation. The NSRCs (Nanoscale Science Research Centers) and other national facilities could be utilized to make and analyze these types of samples. Even more important is the need for new mechanical measurement tools for real time in situ testing. Such tools should be capable of being transported between analysis facilities without damaging samples. The first steps have been taken by several groups in developing MEMS-based mechanical tensile test structures for measuring thin films, nanotubes and nanowires. This work should be fostered to come to fruition and utilized to correlate mechanistic behavior to stress–strain relationships in multiscale modeling.

3.5. The relevant scales

Problems of interest in plasticity, fracture and material behaviour with specific attention to the dominant spatial scale are discussed in this section.

3.6. Meso and connection to continuum models

Several features are of interest at the mesoscale. Several topics are of new or renewed interest because there is a need for a better understanding that will allow constructing predictive physical models. This is the case in particular for:

- Dislocation patterning in monotonic and cyclic deformation, a controversial problem (Kubin, 1993) that can now be approached by both 3D mesoscale simulations (Schwarz et al., 2001; Ghoniem et al., 2000; Zbib et al., 1998; Madec et al., 2002, 2001) and the recent statistical continuum theories of dislocations (El-Azab, 2000).
- Mesoscale models are presently dealing mostly with single crystals deformed in monotonic deformation. They have to move toward more complex materials deformed under more complex conditions (Cleveringa et al., 1997; Lemarchand et al., 2001; Zbib et al., 2002), starting with Bauschinger tests (Thakur et al., 1996a,b), cyclic deformation (Kassner et al., 2000), and rate and temperature effects (Nemat-Nasser, in press).
- Assessing how far the existing mesoscale models, which are based on elementary mechanisms and discrete dislocations, can be extended in terms of the maximum achievable strain. It should be determined whether they can they be used in large strains or will it be necessary to develop new approaches to deal with very large dislocation densities and strongly patterned microstructures.
- Two problems are connected to the previous point. The first is that of improving the physical content of the constitutive formulations used to describe manufacturing processes. The second is that of modeling plasticity in evolving microstructures, moving grain boundaries for ultrafine grained polycrystals, grains refinement at very large strains, precipitation and precipitate dissolution, etc.
- Crack nucleation and evolution, at the meso scale, in brittle and ductile materials needs further investigation. Some progress was made in this regard by employing finite elements with cohesive laws (Zavattieri and Espinosa, 2001). Still, prediction of multiple-cracking in solids accounting for microstructure and statistical fluctuations in strength requires further developments.

There is a renewed interest in large-strain modeling because of the lack of robust and accurate predictive physical modeling of plasticity in evolving microstructures, which is an issue in manufacturing processes, formability, etc. Discrete dislocation models in their current form do not properly address large deformations, anisotropy, etc.

An important example of an unresolved mesoscale issue is that of *grain-size strengthening in metals*. The *Hall–Petch relation*, which describes a hardening proportional to the inverse of the square root of the grain size, is very well verified to very small grain sizes (typically a few nm, but with a strong influence of material processing, as illustrated by Fig. 17). Nevertheless, existing models in terms of dislocation mechanisms (Friedel, 1967; Ashby, 1970; Estrin, 1996) are not mutually

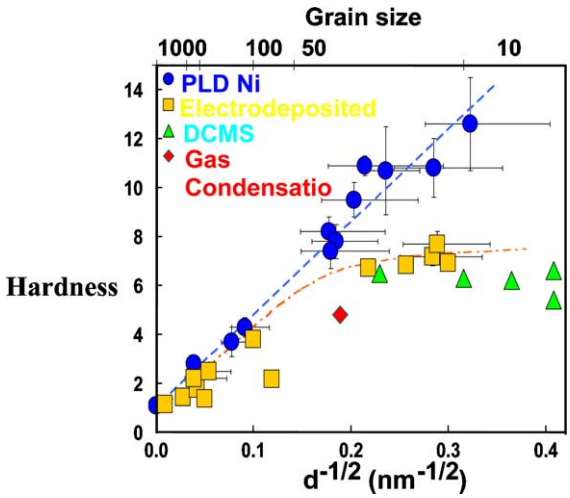

Fig. 17. Hall–Petch model prediction of hardness as a function of grain size and experimental measurements in Ni. Breakdown of the model, as a function of material processing, is not properly understood.

consistent and need to be revisited in order to establish a unified model valid from the onset of yielding up to large strains. Several transitions might be expected on approaching small grain size including nucleation of perfect and partial dislocations, between multiplication in volume and at grain boundaries and deformation mode competitions between dislocation and twinning that do not appear to affect the characteristic scaling relationship, nor the value of the Hall–Petch constant.

3.7. Nano and connection to larger scales

There are several specific mechanistic issues that need further investigation, at the nanoscale which depend upon both computations and appropriate measurements.

- Verification of computational results at the atomic scale by physical measurements.
- Nucleation of dislocations/defects.
- Transition mechanisms such as diffusion, phase transformation, twinning, grain boundary processes, interface/surface effects, confinement effects.
- Mechanisms for crack initiation, including fatigue cracks.
- Dislocation core effects in specific materials.
- Nanostructure design (necessary and not impossible; mechanics can have a big impact by controlling defect generation, can lead to new manufacturing technologies).
- Ab initio simulations of larger systems, although simulations are limited by computer power.
- Surface effects, roughness, surface plasticity, stiction.
- Basis of Hall–Petch, understanding small grain materials (<μm) which is critical for nanoscale systems as well as in plasticity in evolving microstructures.
- Role of defects in small scale structures, such as nanotubes and nanowires.

The *quantification of results from atomistic simulations* for use in mesoscale models is a very high priority. This requires that the atomistic simulations be performed systematically and under well-defined boundary conditions. Likewise, new mathematical algorithms and software are required. Atomistic simulations of large systems are of limited value without a proper physical verification of the outcomes.

The *nucleation of dislocations* in small dislocation-free volumes of crystals is becoming a critical problem in several different situations. This includes the nucleation of dislocations at crack tips that may affect the brittle-to-ductile transition and the low temperature fracture toughness; the nucleation of dislocations under a nanoindenter; the dislocation emission from grain boundaries in nanocrystals or from free surfaces (see Fig. 18), slip steps, and scratches (Brochard et al., 2000; Van Vliet et al., 2003). These processes are relevant to the atomic scale and the nucleation of dislocation loops has to be considered both as a homogeneous or as a heterogeneous process, occurring at kinks, ledges, and wedges. The objective should be to provide criteria predicting, preferably in three dimensions, the critical nucleation conditions. If possible, these should also discriminate between the different possible slip planes on which dislocation may glide. Trans-

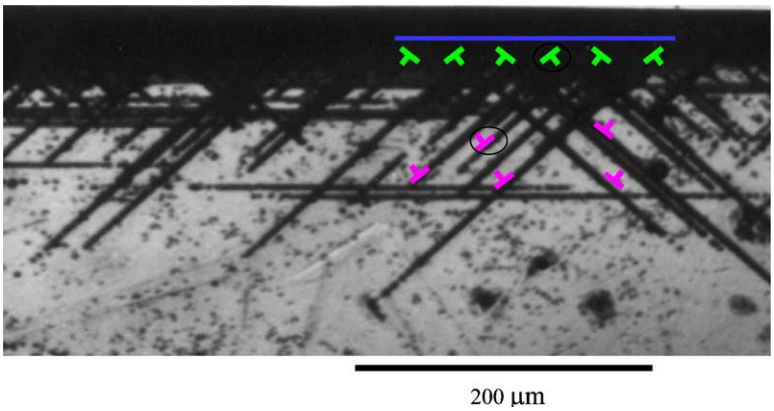

Fig. 18. Example of dislocation nucleation on an atomically smooth MgO single crystal surface.

lating such criteria into mesoscale models will significantly expand the range of problems that can be investigated at this scale. Furthermore, understanding and controlling defect generation are very important. Such control is often necessary in manufacturing (e.g., microelectronics) where defects must be minimized. Conversely, controlled defect nucleation may provide new manufacturing technologies, such as nanoimprinting and embossing.

Again, another unresolved issue, is that of *grain-size strengthening in metals*. The focus for scientists today should be to understand the limits of the applicability of certain mechanisms in order to identify where new mechanisms begin to dominate for nanoscale structures and nanostructured materials. This could lead to a new set of deformation-mechanism maps that are more applicable to nanoscale systems where the surface and interface forces become more dominant than at the macroscale. A prototypical example of bridging this understanding from the macro to nanoscale (old to new) is that of understanding the breakdown of the Hall–Petch relationship, as discussed above. Atomistic simulations of nanopolycrystalline materials with grains of a few tens of a nanometer, are being performed. These are beginning to provide information regarding the crossover between dislocation glide, twinning and grain boundary sliding and twinning (Yamakov et al., 2002, 2003; Van Swygenhoven, 2002; Schiøtz and Jacobsen, 2003).

3.8. Moving forward

Dislocation core effects, lattice friction (the Peierls stress) *and consequences on dislocation mobility* by kink-pair mechanisms have long been recognized as subjects that require an atomistic understanding. Investigating the details of the plasticity of bcc transition metals, intermetallic alloys, some transition hcp metals such as Ti, Zr, semi-conducting materials and ceramics immediately focuses attention to the dislocation cores and to effects of the atomic bonding. Appropriate mobility laws for dislocation motion must be derived from such investigations. This continues to be a very important area of research particularly because chemical sensitivity and material specificity can only be incorporated in descriptions of plasticity through dislocation core effects and the details of the atomic bonding. Both atomistic simulations employing empirical interaction models, but particularly semi-empirical tight binding methods and ab initio simulations, which are just now becoming available for the study of such problems are needed (Woodward and Rao, 2001; Yang et al., 2001; Pérez and Gumbsch, 2000; Beckman et al., 2002). *New quantum mechanical methods* are emerging, which allow systems to be treated in "real" space and allow for the application of complex boundary conditions. Furthermore, *hybrid simulation methods* allow seamless incorporation of quantum mechanical accuracy into atomistic simulations in small regions. Such methods have enormous potential in

providing the much-needed chemical specificity in the studies of elementary defects.

3.9. Concluding remarks

The following areas in which mechanics is of relevance and areas in which mechanics plays a leading role.

Areas in which mechanics has made significant inputs/contributions, but where a (potential) leadership role is not generally acknowledged:

(1) Microelectronics reliability issues, aging; control of manufacturing;
(2) Nano- and meso-manufacturing and sensor design;
(3) Lightweight structure technology;
(4) Microimprinting and embossing;
(5) Protective coatings.

Areas in which mechanics has leadership:

(1) Failure, fragmentation, fracture, brittle to ductile transition, blast resistant structures.
(2) Safety and reliability issues.
(3) Mathematical modelling, including analytical solutions and multiscale computational algorithms.
(4) Bridging from basic understanding to predictive codes/models.
(5) Bottom-up approaches in nanotechnology.

Lightweight material/structure technology has always been in high demand and has spawned recent developments of new material microstructures such as amorphous metals, intermetallics, nanostructured materials and various multiphase materials. New applications, driven in the past largely by aerospace designs, are being developed for lightweight computers, cellular phones, energy storage systems, automobile components, ship and other naval structures, armor, etc. Mechanics has a leadership role in these areas.

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