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Materials aging at the mesoscale: Kinetics of thermal, stress, radiation activations

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ABSTRACT

The complexity of materials aging may be seen as a result of the interplay between several activation processes operating on multiple spatial and temporal scales. Though the disciplines involved may seem disparate at first, material aging fundamentally could be linked by the same set of underlying activations and responses of the system. We examine how recent studies of shear-induced deformation and rheological flow initiated in the soft-matter community can be leveraged to probe the mechanisms of radiation damage in nuclear materials. Bridging these two traditionally separate areas of research demonstrates the emerging notions of mesoscale science as a research frontier concerned with linking macroscale behavior to microscale processes in driven systems. We suggest the combining of microstructure-sensitive measurements with fundamental theories and mechanism-specific simulations is essential to addressing metastable materials responses of strongly activated states.

The mesoscale science frontier

In the past two years a frontier for materials research at an intermediate regime between microscopic and macroscopic scales has emerged with the prospect of scientific advances coupled with technological impact [1–3]. Many types of materials are known for their functional behavior on the macro-scale. In these systems the molecular interactions also have been thoroughly studied. What is missing is a quantitative understanding of the mechanisms underlying the cause-effect relation between molecular interactions and functional behavior. If such connections could be established, it would enable materials behavior at the *systems level* to be optimized by knowledge-based manipulation at the *micro- and mesoscopic levels*. The bridging of the *micro–macro gap* is the essence of the Mesoscale Science (MSS) frontier.

Since the initial recognition of the "the middle way" as a missing conceptual link [4], there have been extensive discussions of the many facets (hallmarks) of MSS, and the different problems that illustrate the breadth of this fundamental notion [2]. These efforts notwithstanding, MSS remains an open-ended idea inviting further definition, scrutiny, and demonstration of its merits. It is in this spirit that we offer additional characterization of this scientific frontier and a perspective focused on time-dependent materials deformation.

While a single organizing principle capable of defining MSS seems to be an unlikely prospect, we believe it is nevertheless appropriate to recall the discussions surrounding the formulation of a unifying concept in non-equilibrium statistical mechanics known as *self-organized criticality* (SOC) [5–7]. The hypothesis of SOC was that very different physical systems, ranging from sand dunes to spring networks to even stock markets, are driven by a combination of external forces and internal interactions to special ('critical') states of the system. These states have universal character in that their statistical properties show power-law scaling with the same exponents, the implication being their temporal evolutions are not controlled by any single event. SOC attracted broad interest in the physics community because it appeared to provide a general measure of system complexity involving two concepts, one of self-organization and the other of critical behavior, each with its implications regarding how natural phenomena evolve in time. Since a precise mathematical formulation of SOC in non-equilibrium statistical mechanics is still not available [7], it appears reasonable not to expect anything different in looking for new underlying principles governing MSS. This is in contrast to the principles underlying the free energy or the partition function in thermodynamics, which may be considered the equilibrium counterparts to SOC [7], or perhaps to MSS. On the other hand, SOC and MSS should share their reliance on threshold (metastable) behavior and the dominating influence of fluctuations. In particular insights from SOC remind us of the importance of self-organizing processes in describing the microstructure evolution relevant to

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MSS. For example, the presence of rate-dependent response to a driving force, or memory effects, is a hallmark of MSS. These rate-dependent processes are often governed by long-range interactions between defects on two major length scales, one pertaining to the constituent particles of the system (microscale), the other to activated complexes or defect clusters (mesoscale).

We see in MSS an emphasis on microstructural defects that result from the combined effects of strong internal molecular interactions and external driving forces. Referring to them as *self-organized defects* (SOD), we propose the characteristic spatial–temporal scales on which they evolve should define the relevant scales for MSS. The SODs, once formed, will not likely evolve in isolation in any realistic scenario; rather they will self-organize to further multiply or agglomerate, triggering larger-scale structures displaying their own metastable behavior in the presence of an activated environment. Thus, a characteristic behavior of MSS is a system which is evolving in a continuous state of activation. What are examples of such defects, and what is meant by their evolution? While we provide illustrations in the following discussions of yielding in soft matter and radiation damage in nuclear materials, these are also the questions to motivate future research in MSS.

Nonlinear rheology of soft matter

Colloidal dispersions represent one of the simplest classes of materials for which the interplay between dynamical behavior of dense fluids and externally controlled flow can be investigated. As soft matter they also have widespread applications in all forms, plastics, paints, slurries, etc. [8,9]. A basic challenge in nonlinear rheology is to relate the microscopic structure and dynamics to the macroscale stress and flow behavior. Above a certain packing fraction, dense colloidal fluids are expected to display a yield stress and a time delay in hydrodynamic diffusion. Similarly, the onset of flow beyond a critical shear strain is generally attributed to the breaking up of local cages surrounding each particle, and correlated particle rearrangements. Microstructure evolution characteristics like these make the study of nonlinear rheology a research enterprise in which experiments, theoretical modeling, and particle simulations play complementary roles. The advantage of combining experiments with theory and simulation is that one can probe more fully the relation between the macroscale behavior and the underlying mechanisms at the microscale. By this we mean molecular-level details that theory and simulation can provide are useful for interpreting time-dependent macroscale measurements, which by themselves provide insufficient insight to the underlying microstructure evolution. An area in which this awareness is beginning to emerge is the study of chemical structure and mechanics of cement. A molecular model of the binder phase of cement paste is being developed [43] as a basis for interpreting various measurements of structural and physical properties [44,45]. At stake is the link between microscopic simulations and macroscale behavior, and the ability to optimize the design of the binder for durability and environmental impact [46].

Two recent attempts to quantify the micro–macro relation illustrate the benefits of integrating a triad of research capabilities. First, the onset of yielding during start-up shear was investigated by subjecting suspensions of PMMA particles (267 nm and 788 nm in size) to rheometry and confocal microscopy measurements combined with Brownian particle dynamics simulations [10]. Then the onset of stress relaxation in a flowing suspension when shear rate is abruptly switched off was analyzed by a highly sophisticated theoretical analysis in conjunction with molecular dynamics simulations, in addition to macroscopic rheological measurements [11]. In complementary ways both studies exemplify the essence of microstructure evolution on the mesoscale.

Fig. 1 shows the stress–strain variation at several shear rates, expressed in terms of the Péclet number, $\mathrm{Pe} \sim \dot{\gamma}\tau$, where $\dot{\gamma}$ is the shear rate, and τ is a relaxation time. Each measurement gives a peak (yield) stress σ_y and a corresponding strain γ_y. A higher yield stress is obtained with increasing shear rate, a behavior known as stress overshoot. Note also that the yield strain increases with the shear rate.

A qualitative interpretation of the yielding behavior shown in Fig. 1 suggests a certain amount of time is needed for the colloidal particles to align themselves in response to the imposed shear. This would be an indication of memory effects. Intuitively one expects that if the shear rate is too fast for the process to complete, then the system will act more rigidly and with a time delay. This can be regarded as a general consequence of rate or 'memory' effects associated with microstructure evolution. The system response should also depend on the amount of space locally available to the particles, or at the macroscale on the free volume (packing fraction) in the system. This simply means microstructure evolution has corresponding manifestations in the spatial and temporal degrees of freedom. An example of the equivalence can be seen in Fig. 2, in the form of the flow curves at two packing fractions (2(a)), and the yield stress variation with the packing fraction, Fig. 2(b) [12]. If one were to ask about the underlying mechanisms of yielding according to a theoretical description, or about direct particle simulation on the same scales as the measurements, then the results for such discussions have become available only recently.

In viscous liquids or dense suspensions a typical mode of atomic motion is the rattling of a particle temporarily confined in a cage formed by its near neighbors [13]. These vibrations are transient since the cages form and breakup spontaneously, their lifetimes being determined by the local configurational environment, the interparticle interactions, and the forces of thermal and stress activations. The presence of the caging effect is directly reflected in the time variation of the velocity autocorrelation or the mean-squared displacement function, which are quantities that can be extracted from scattering experiments or computed from molecular simulations [14].

Fig. 3 shows the mean squared displacement obtained in a molecular dynamics simulation of water molecules in a porous silica gel, at density 0.5 g/cc and a temperature of 100 K [14]. The initial low values of MSD indicate the molecules (on average) are trapped in a cage with a lifetime of ~50 ps. after which they undergo diffusive displacements (MSD ~ linear in tine) until a second cage is formed approximately 50 ps later. A Voronoi tessellation of the particle coordinates, shown in the inset, provides confirming evidence that the different neighbor configurations are involved in the two trapping events. At lower temperatures

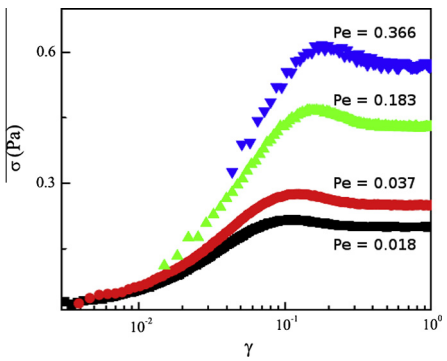

Fig. 1. Rheometry data on yielding of a colloidal (PMMA) glass under shear showing stress overshoot and yield-strain shift with shear rate (expressed in Péclet number) [10].