

Multiscale materials modelling at the mesoscale

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The challenge to link understanding and manipulation at the microscale to functional behaviour at the macroscale defines the frontiers of mesoscale science.

Over the course of the past decade, the impact of computation on materials research has expanded dramatically. A number of panel reports^{1–6}, workshop and conference proceedings, handbooks and monographs^{7,8}, all point to the promise of multiscale materials modelling and simulation. The broad community of materials research has also seen the formation of strategic alliances aimed at technology breakthroughs that have been made possible by emerging modelling and simulation capabilities driven by high-performance computing. A central issue that invariably comes up in all the discussions is how the understanding of mechanisms at the microscale can

enable predictions of functional behaviour at the macroscale. Although this is a challenge that has not gone unnoticed, see for example ref. 9, a new awareness has recently emerged on the notion of linking the micro- to the macroscale.

In 2012, the Office of Science, part of the US Department of Energy, initiated a dialogue with the science community through a series of town-hall meetings, the purpose being to identify new science frontiers at the mesoscale¹⁰. A website (www.meso2012.com)⁴ was established to solicit community input. A report, *From Quanta to the Continuum*, has been released⁴ along with an overview of the findings relevant to the materials

community¹¹. (Reference 4 is particularly relevant in that it gives a complete account of the broad community discussions of strategic research that connects materials science and engineering at the science and technology community at large.) It seems that ‘mesoscale science’ (MSS) should be viewed as an open concept, the principles of which are not precisely specified until a problem context is established. In other words, MSS can be characterized in many different ways. An early approach looked for organizing principles governing certain phenomena, such as energy landscape descriptions of transition states, self-organization and dynamical feedback, and frustration (or localization) effects, known

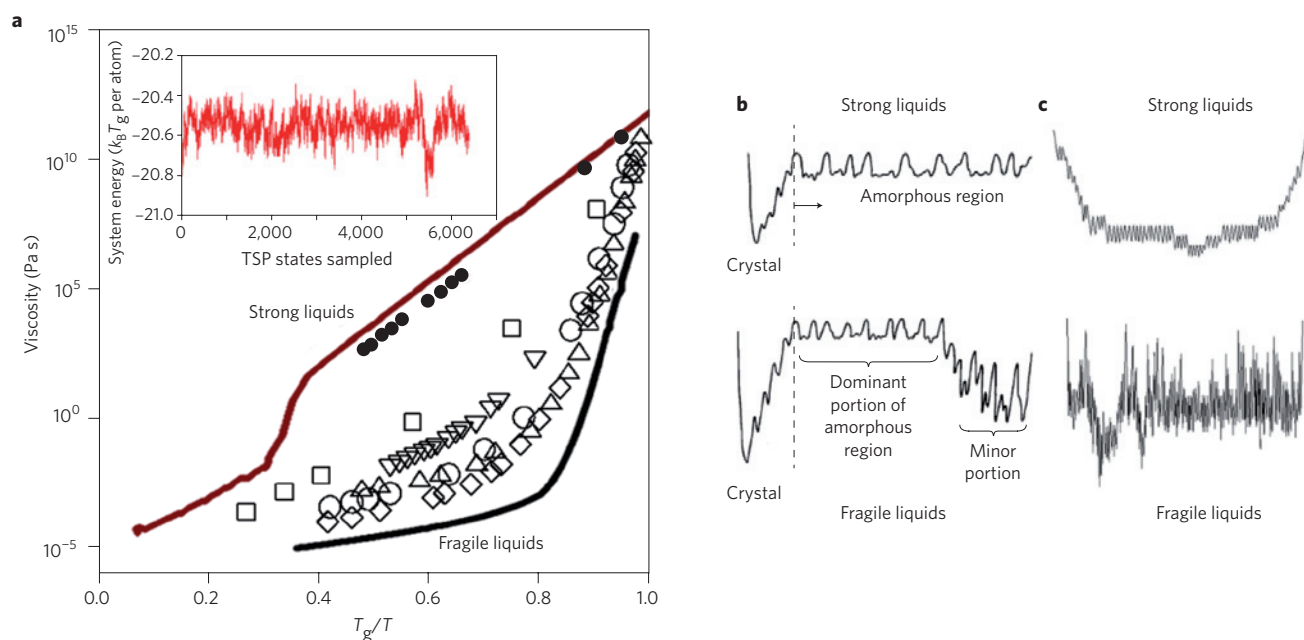


Figure 1 | Temperature variation of shear viscosity of a supercooled liquid. **a**, Experimental data on SiO_2 (filled circles) and fragile glasses (open symbols)¹³, and corresponding theoretical calculations (solid curves)^{15,16}. The glass transition temperature, T_g , is defined here as the temperature at which the viscosity has the value of 10^{12} Pa s. Inset: TSP trajectory sampled using a metadynamics algorithm¹⁴. **b**, Conceptual sketch of potential-energy profiles for strong and fragile liquids¹⁹. **c**, Actual profiles deduced from TSP trajectories like that from panel **a**¹⁵. Figure reproduced with permission from: **a**, ref. 13, © 1988 Elsevier; inset, ref. 14, © 2009 AIP; **b**, ref. 19, © 1988 AIP; **c**, ref. 15, © 2009 AIP.

to be important in the statistical physics or biophysics domains¹². This could be considered a top-down view. A more recent approach, which takes a bottom-up view, focuses on discrete particle systems to identify local spatial and temporal features, such as activated processes, dynamically heterogeneous environments, intermittency and 'rare' events¹¹. To promote further discussions, we offer here three materials phenomena as candidates for quantifying MSS in the area of materials ageing and environmental degradation.

Materials challenges at the mesoscale

The strong variation of the shear viscosity of supercooled liquids with temperature (Fig. 1) is a signature of slow dynamics, a characteristic phenomenon fundamental to our understanding of the glass transition. Two broad classes of behaviour are shown, an Arrhenius variation (filled circles) for an oxide glass such as SiO₂, and a distinctly non-Arrhenius variation (open symbols) for several molecular glasses¹³. The latter, known as 'fragile' scaling, is the more intriguing, as it indicates a thermal activation process where the activation barrier is temperature dependent. How to explain the so-called fragile behaviour using only atomistic concepts has been a topic of enduring interest in the glass science community.

Figure 1 also shows that the experimental data can essentially be explained by calculations^{14–16} (curves in Fig. 1a). Because these curves can be obtained using information exclusively provided by atomistic simulations, they provide a way to understand the nature of fragility in supercooled liquids in terms that are, in effect, quantifiable. According to classical transition-state theory, the shear viscosity of a glassy liquid can be expressed as¹⁷

$$\eta(T) = \eta_0 \exp[Q(T)/k_B T] \quad (1)$$

where η_0 is a reference viscosity value generally known or accepted, $Q(T)$ is an effective activation barrier, k_B is the Boltzmann constant and T is the temperature. Within this description, understanding the behaviour of $\eta(T)$ amounts to an explanation of $Q(T)$. The essential ingredient needed to calculate the curves in Fig. 1a is the trajectory of the transition-state pathway (TSP), which is information obtained by sampling the potential energy landscape^{14,18}. An actual trajectory for a fragile glass model is shown in Fig. 1a. It is an alternating sequence of local energy minima and saddle points (transition states), and associated with

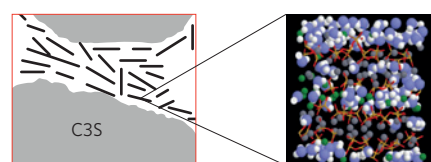
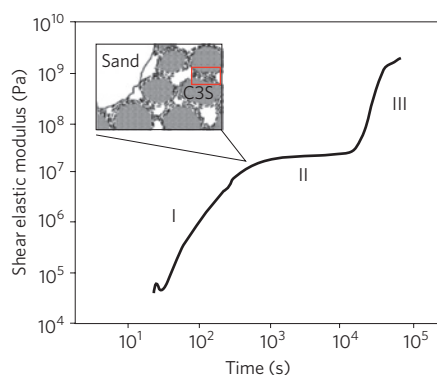


Figure 2 | Time evolution of complex shear modulus in a cement paste measured by an ultrasonic method. Data from ref. 26. Inset: schematic of cement hydration — dissolution of clinker C3S grains and precipitation of C-S-H (black bars)²⁷. Bottom left: magnified version of area enclosed by red box in inset. Bottom right: molecular model of C-S-H showing the arrangement of CaO layers, SiO₂ chains and water molecules³¹. Blue and white represent oxygen and hydrogen atoms of water, respectively, green and grey denote inter- and intralayer calcium ions, yellow and red represent silicon and oxygen atoms in silica tetrahedra. Figure reproduced with permission from: inset, ref. 27, © 2005 ACS; bottom right, ref. 31, © 2009 NAS.

each are the known positions of all the particles in the system. A trajectory thus specifies the path of the system as it evolves by moving on its potential energy landscape. These physical details are then processed by statistical analysis and coarse graining to give $Q(T)$ (refs 14,15). The TSP trajectory can be used to directly calculate $\eta(T)$ through linear response theory¹⁶ without using equation (1). Such information also elucidates our notion of the energy landscape description of amorphous media. It has been suggested¹⁹ that the potential-energy surface associated with Arrhenius ('strong') temperature dependence should be relatively smooth, whereas the energy surface giving rise to fragile behaviour should be quite rough, as depicted schematically in Fig. 1b. Figure 1c displays the actual surface profiles deduced from the TSP trajectories¹⁵, which provide a quantitative measure of the respective landscape topologies. From the computational

standpoint it is worth noting that probing glassy dynamics requires simulation at the mesoscale, because the timescale relevant to the experimental data lies well beyond the capability of conventional simulation techniques at the microscale. The thermal activation processes observed in the high-viscosity region in Fig. 1a can be regarded as rare events in the context of materials modelling and simulation at the microscale.

The onset of a sharp increase in $\eta(T)$ over a small temperature range is characterized by a crossover (or critical) temperature T_x (T_c) (ref. 20). What could be the change in the atomic configurations or interatomic interactions underlying such an upturn, or kink behaviour in the temperature variation? As a result of the calculations^{14–16}, the increase in the resistance to viscous flow (curves in Fig. 1a) can be interpreted as showing that the system is becoming intermittently trapped in deep energy basins. In the energy landscape framework the crossover phenomenon — the transition from gradual to accelerated variations in behaviour — can be expected whenever different existing mechanisms compete, and the dominance of one over the other depends on the local environment or driving force. Consider an analogy between viscous flow in glassy fluids and creep deformation in plastic solids. Although glass rheology and crystal plasticity are seldom regarded as closely related phenomena, it has recently become appreciated that transition-state theory, as described by equation (1), is equally suitable in describing stress-driven responses where $Q(T)$ is replaced by a stress activation barrier $Q(\sigma)$. Such an approach is capable of describing a sudden upturn behaviour in the variation of yield stress with strain rate²¹, which may be compared to the variation in viscosity with inverse temperature of the fragile liquids shown in Fig. 1. This upturn or kink variation is a characteristic dynamical response seen experimentally in systems from metals²² to colloidal suspensions²³. Its widespread presence suggests a simple underlying origin, basically a localization (or confinement) process. Thus the crossover in $\eta(T)$ would correspond to stress localization as the system is trapped in a deep energy basin, whereas the crossover in the yield stress would correspond to strain localization when the strain rate reaches a critical value. Whether there is a common underlying origin in the different physical behaviour²⁴ is a question for the development of MSS.

In our second illustration of MSS, we focus on a specific system, cement. As the

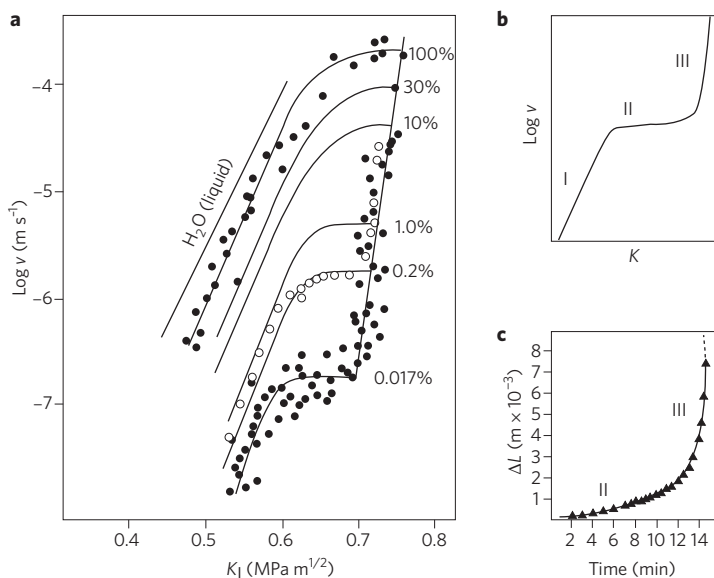


Figure 3 | Data and schematics showing upturn behaviour in fracture toughness curves of glasses exposed to different moisture levels. **a**, Variation of crack propagation speed in soda-lime silica glass with applied tensile stress K_I measured at various moisture levels. **b**, Schematic showing the behaviour of $v(K)$ that has three distinct stages of evolution (see main text for explanation)³⁴. **c**, Time evolution of measured crack length (ΔL) showing that it corresponds to the expected behaviour of stages II and III (ref. 33). Figure reproduced with permission from: **a,c**, ref. 33, © 1967 Wiley.

most widely used structural material on Earth, concrete is irreplaceable in terms of commercial availability and widespread utility. The scientific challenge of concrete lies in understanding the mechanisms of setting (hydration)²⁵, the process by which cement paste, a mixture of cement powder and water, becomes hardened over time. Hardening can be measured directly by an ultrasonic probe that gives the time evolution of the complex shear modulus, as shown in Fig. 2 (ref. 26). The rigidity of the paste rises to a level of ~ 10 MPa on the order of minutes, stays relatively constant over a few hours, and then rises sharply to several GPa overnight. Unlike the viscosity behaviour shown in Fig. 1 where calculations can be directly compared to experiments, it is not yet feasible to fully analyse the setting curve of cement paste shown in Fig. 2, or its counterpart, the hydration curve²⁵. There is consensus in the cement and concrete research community that setting is a key challenge with significant potential for innovation, for example, in the development of additives. Our qualitative understanding of cement setting begins with (1) clinker dissolution causing precipitation of the hydration product calcium silicate hydrate (C–S–H, or $\text{CaO-SiO}_2\text{-H}_2\text{O}$; inset of Fig. 2; ref. 27), (2) growth of the C–S–H phase, and (3) hardening of the evolving paste²⁸. The latter two stages are especially

lacking in mechanism-based analysis. To address mechanical behaviour from the standpoint of C–S–H growth, one needs to understand how the hydration products affect the packing fraction²⁹, and the formation and evolution of pores³⁰, in processes such as the kinetics of dissolution and precipitation (nucleation and growth), the percolation (or jamming) of the emerging network of C–S–H, and the effects of water in the interlayer regions of C–S–H and in the pores. All these can be considered examples of MSS challenges with significant industrial implications². At the microscale, a molecular model of C–S–H, which is chemically consistent with neutron scattering measurements (Ca/Si ratio and water density), has been proposed³¹ (Fig. 2). It remains an open problem to introduce such atomic-level details in multiscale materials modelling studies to achieve a predictive capability for cement setting³².

Yet another way to identify mesoscale science challenges in the materials domain is to consider an interdisciplinary phenomenon. Stress corrosion cracking (SCC), a technologically important process in the area of environmental degradation of materials, is our third illustrative example. The relevant functional behaviour here is the variation of crack velocity with applied stress. Figure 3 shows experimental data on static fatigue, where crack propagation in

glass specimens under tensile loading was studied with respect to varying moisture levels in the environment³³. Figure 3 is similar to Fig. 2 in that the interpretations of the macroscale experimental data in terms of underlying mechanisms and processes at the mesoscale are not yet feasible. To facilitate interpretation and guide the eye, lines at six constant moisture levels have been fitted through a large collection of data, only a subset of those at 0.017% and 100% are shown as filled circles. Additionally, the data from a single run at 0.2% are shown as open circles. The variation of crack propagation speed with applied stress $v(K)$ is seen to follow a three-stage response³⁴, a schematic of which is shown in Fig. 3b. There is a resemblance to the microstructure evolution in the three-stage setting of cement paste (Fig. 2). Keeping in mind that both chemistry (corrosion) and mechanics (stress) play a role that is manifest in Fig. 3, we may regard the onset of crack propagation at low stress (stage I) as a threshold effect of corrosion-induced bond breaking. The rapid increase of $v(K)$ indicates a strong stress-dependence as well as sensitivity to the environment. Stage II in Fig. 3b is characterized by the crack speed becoming stress-independent (compare with stage II in Fig. 2). This may be a consequence of the rate-limiting process of water diffusing to the crack tip, just as the formation of C–S–H in cement limits the rate of cement curing. It would be interesting to probe this region further to clarify the interplay between local reactivity and spatially extended transport. More generally, this coupling is fundamental for identifying the hallmark character of the slow dynamics of SCC. In stage III, the propagation curve reverts back to a second threshold behaviour, now with brittle fracture controlled by the Griffith criterion with corrosion playing at most a minor role. To emphasize the delayed nature of SCC, Fig. 3c explicitly shows the increase in crack length to the critical point of failure on the timescale of observation. Correlating this direct evidence with the ‘mechanism map’ in Fig. 3b will enable one to understand the importance of controlling the growth rate and avoiding the occurrence of a critical crack length³⁵. Identifying a definitive link between atomistic-level bond breaking or crack formation and a measurable crack speed at the macroscale therefore presents an opportunity for contributions by MSS.

Implications for mesoscale science

Collectively, the macroscale behaviour of glass viscosity, cement setting and

SCC illustrate the capability of MSS to incorporate a range of materials phenomena such as ageing and durability. There are clearly other cases of functional behaviour in need of mesoscale analysis and interpretations. The experience gained in the sampling and analysis of TSP trajectories in understanding viscous flow in glassy states could be useful in other problems. The challenges of quantifying C–S–H nucleation and growth in cement setting, and the interplay between chemical attack and stress-driven cracking in delayed fracture in glasses all provide opportunities for developing TSP sampling methods to reach experimental timescales (Fig. 2 and Fig. 3c).

The underlying physical phenomenon common to the problems we have highlighted is the evolution kinetics of the mesoscale structure. By this we mean the time-dependent relationship between the evolving ‘defect’ configurations at the mesoscale (for example, glassy configurations, granular assembly of C–S–H and propagating crack tip) and the corresponding functional properties (viscosity, shear modulus and crack speed) at the macroscale. This correlation is an extension of the familiar structure–property correlation, which has been a longstanding paradigm of materials science. The novelty in the present context is dealing with the cross correlations, linking different sets of degrees of freedom associated with different spatial and temporal scales. Although cross correlation has always been part of the spirit of multiscale materials modelling, even in the early days⁹, quantitatively understanding this correlation in specific problems of broad interest could expand the scope of MSS in new directions.

It seems entirely appropriate MSS should play a key role in the quest for coupling scientific advances with technological impact. We also see MSS as the enabling capability essential to strategic alliances, particularly concerning the reliability and optimization of materials. In 2010, the US Department of Energy established an Energy Innovation Hub on nuclear modelling and simulation, the Consortium for the Advanced Simulation of Light Water Reactors (CASL)³⁶. Among the ongoing CASL research projects is an effort to better understand and control corrosion in nuclear reactors³⁷. The formation and growth of the corrosion product known as chalk river unidentified deposits (CRUD) on fuel rods, for example, is similar in complexity to the precipitation and growth of C–S–H in the cement setting process. Understanding the properties of CRUD

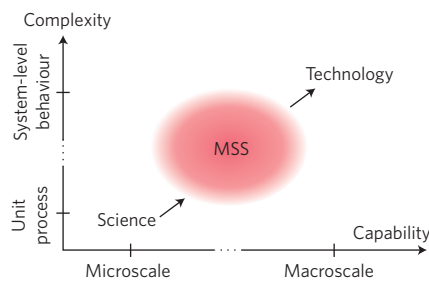


Figure 4 | Complexity–capability map showing the separation between scientific studies at the microscale and technology innovations at the macroscale along the capability axis. The separation between unit processes associated with isolated mechanisms and integrated system-level functional behaviour is shown along the complexity axis. Bridging the gaps will require the development of modelling, simulation and experimental capabilities in the mesoscale realm to address the relevant functional behaviour extending to the macroscale.

requires treating the phenomena of heat transfer, fluid flow, chemistry, precipitation and dissolution, and the underlying corrosion of the fuel cladding in a coupled manner³⁸, a problem that is much too complex for microscale modelling and simulations alone. Indeed, CRUD is more challenging than the cases we have considered because, in addition, coupled radiation and neutronic effects are now involved. With CASL being a partnership of national laboratories, industries and universities, solving a problem such as CRUD would demonstrate the importance of teamwork among the stakeholders, in particular, partners from industry. Overall the MSS concept should be applicable to any field where scientific capabilities and technology innovations overlap at the mesoscale (Fig. 4). The gap between the science push and technology pull is an inherent part of scientific exploration and discovery. How to bridge this gap is worthy of our future efforts. □

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