SIMULATIONS OF MECHANICS AND STRUCTURE OF NANOMATERIALS — FROM NANO SCALE TO COARSER SCALES

J. Schiøtz*, T. Vegge, F. D. Di Tolla† and K. W. Jacobsen

Center for Atomic-scale Materials Physics and Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark.

*Also at: Materials Research Department, Risø National Laboratory, DK-4000 Roskilde, Denmark.

†Present address: SISSA, Via Beirut 2–4, I-34014 Grignano (TS), Italy.

ABSTRACT

We discuss how simulations of mechanical properties of materials require descriptions at many different length scales — from the nanoscale where an atomic description is appropriate, through a mesoscale where dislocation based descriptions may be useful, to macroscopic length scales. In some materials, such as nanocrystalline metals, the range of length scales is compressed and a polycrystalline material may be simulated at the atomic scale. The first part of the paper describes such simulations of nanocrystalline copper. We observe how the grain boundaries contribute actively to the deformation. At grain sizes below 10–15 nm deformation in the grain boundaries dominate over the traditional dislocation-based deformation mechanisms. This results in a reversal of the normal grain size dependence of the yield stress: we observe that the material becomes softer when the grain size is reduced. The second part of the paper gives an overview over simulation techniques appropriate for problems too large to be treated in atomic-scale simulations. It also describes how different simulation techniques can be combined to describe the interplay between phenomena at different length scales through multiscale modelling.

1. INTRODUCTION

In the last decades the development of larger and faster computers has progressed at a tremendous rate, doubling the capabilities of a typical computer every 18 months. This development has enabled the field of “computational materials physics” to contribute significantly to the understanding of materials and their properties. In this paper we focus on the modelling of mechanical properties of nanocrystalline metals, i.e. of metals with a grain size in the nanometer range. The
main focus is on atomic-scale simulations, but we also look at other simulation techniques for modelling materials at coarser length-scales.

As matter is made of atoms, and as the quantum mechanical equations governing the interactions of atoms (and the associated electrons) are known, one could imagine that it is — at least in principle — possible to solve these equations and predict the properties of matter from first principles. For simple properties of single-crystalline defect-free metals this is indeed possible. With quantum mechanical methods one is, however, only able to treat up to a few hundred atoms, and even there one has to resort to approximations when solving the fundamental equations. When treating complicated processes such as plastic deformation, this is clearly inadequate. One has to give up the ambition of retaining a full quantum mechanical description of the atomic interactions, and describe them by interatomic potentials.

Using parallel supercomputers, one can handle up to $10^8$ atoms for times up to a nanosecond, when the interactions are described using simple pair potentials (Abraham 1997; Abraham, Schneider, Land, Lifka, Skovira, Gerner and Rosenkranz 1997; Bulatov, Abraham, Kubin, Devincre, and Yip 1998), or up to 35 million atoms using more realistic many-body potentials (Zhou, Beazley, Lomdahl and Holian 1997). In most cases one is limited to significantly smaller systems by the need to run a large number of simulations (and often by economical factors as well). The length scale of typical processes in plastic deformation is $1 \mu m$ or more, and the time scale is typically seconds or longer. This corresponds to $10^{11}$ atoms in $10^9$ nanoseconds, requiring a computational power of $10^{12}$ times what is possible today. Even if computers continue to improve at the current rate, such computational power will not become available in a foreseeable future. One is therefore forced to abandon using an atomistic approach to the whole problem, but will have to split up the problem according to the different length scales involved, and reserve the atomistic approach to the processes at the smallest length scales, see e.g. Carlsson and Thomson (1998).

In this paper we will give an overview over how this gap between different length scales can be bridged in simulations of plastic behaviour. In the first part we describe simulations of systems where the characteristic length scales are so small that the entire system can be studied atomistically. The system we have chosen is nanocrystalline metals. In the second part we give an overview of different simulation techniques at the micro and mesoscale, and how the different scales can be combined.

2. ATOMIC-SCALE SIMULATIONS OF NANOCRYSTALLINE METALS

Nanocrystalline metals are metals with grain sizes on the nanometer scale, typical grain diameters range from 5 to 50 nanometers. These materials are of technological interest, mainly because their strength and hardness often are far above what is seen in coarse-grained metals. This is generally believed to be caused by the grain boundaries acting as barriers to dislocation motion: as the grain size is decreased, the number of grain boundaries increase and the dislocation motion becomes harder, leading to a harder material. This grain size dependence of the hardness and the yield stress — the Hall-Petch effect (Hall 1951; Petch 1953) — is observed in coarse grained materials as well as in nanocrystalline metals. It is indeed possible to get a good estimate of the hardness of
Simulations of mechanics and structure of nanomaterials — from nanoscale to coarser scales

nanocrystalline metals by extrapolating from the Hall-Petch behaviour at larger grain sizes. For a further discussion of the mechanical properties of nanocrystalline metals, see e.g. the reviews by Siegel and Fougere (1994) or Morris and Morris (1997).

Nanocrystalline metals are an attractive group of materials to model for many reasons. The materials are interesting from a technological point of view, but also from a theoretical point of view since the small grain size results in a “cut off” of the typical length scales of the phenomena and structures that may appear during the deformation process. This simplifies the deformation process and may possibly facilitate the development of theoretical models. Eventually, it may be possible to extend these models to the more complicated cases of coarse grained materials. For the smallest grain sizes (below approximately 5–10 nm) it becomes possible to model the deformation process directly using atomic-scale computer simulations. The deformation processes may then be studied directly (Schiøtz, Di Tolla and Jacobsen 1998; Van Swygenhoven and Caro 1997a,b).

2.1. Generation of the “samples” We attempt to generate “samples” with a structure reasonably similar to the structures observed experimentally: essentially equiaxed dislocation free grains separated by narrow grain boundaries. The grains are produced using a Voronoi construction. A set of grain centres are chosen randomly, and the part of space closer to a given centre than to any other centre is filled with atoms in a randomly rotated f.c.c. lattice. Periodic boundary conditions are imposed. This procedure generates samples without texture, and with random grain boundaries. In the grain boundaries thus generated, it is possible that two atoms from two different grains get too close to each other, in such cases one of the atoms is removed to prevent unphysically large energies and forces as the simulation is started. To obtain more relaxed grain boundaries the system is annealed for 10 000 timesteps (50 ps) at 300 K, followed by an energy minimisation. This procedure is important to allow unfavourable local atomic configurations to relax. A sample generated in this way is shown in Fig. 1.

To investigate whether the parameters of the annealing procedure are critical, we have annealed the same sample for 50 and 100 ps at 300 K, and for 50 ps at 600 K. We have compared the mechanical properties of these samples with those of an identical sample without annealing, we find that the annealing is important (the unannealed sample was softer), but the parameters of the annealing are not important within the parameter space investigated.

A similar generation procedure has been reported by Chen (1995), by D’Agostino and Van Swygenhoven (1996), and by Van Swygenhoven and Caro (1997a,b). A different approach was proposed by Phillpot, Wolf and Gleiter (1995a,b): a nanocrystalline metal is generated by a computer simulation where a liquid is solidified in the presence of crystal nuclei, i.e. small spheres of atoms held fixed in crystalline positions. The system was then quenched, and the liquid crystallised around the seeds, thus creating a nanocrystalline metal. In the reported simulations, the positions and orientations of the seeds were deterministically chosen to produce eight grains of equal size and with known grain boundaries, but the method can naturally be modified to allow randomly placed and oriented seeds. The main drawback of this procedure is the large number of defects (mainly stacking faults) introduced in the grains by the rapid solidification. The stacking faults are clearly seen in the resulting nanocrystalline metal (Fig. 7 of Phillpot et al. 1995a). Some of
Fig. 1: A simulated nanocrystalline copper sample before (a) and after (b) 10% deformation. The system contains approximately 100,000 atoms arranged in 16 grains, giving an average grain diameter of 5.2 nm. Atoms are colour-coded according to the local crystalline order: white atoms are in a perfect f.c.c. environment, light gray atoms are in a local h.c.p. environment, these atoms are at stacking faults. Atoms in any other environment are coloured dark gray, these atoms are typically in grain boundaries or dislocation cores. In the left side of the system, a partial dislocation is seen moving through a grain, leaving a stacking fault in its wake (arrow in (b)). From Schiøtz et al. (1998).

us have earlier performed simulations of the solidification of a large cluster (unpublished). These simulations have shown that a large number of stacking faults appear even if the cooling is done as as slowly as possible in atomistic simulations.

2.2. The simulation technique. We model the interactions between the atoms using a many-body potential known as the Effective Medium Theory (EMT) (Jacobsen, Nørskov and Puska 1987; Jacobsen, Stoltze and Nørskov 1996). It is very important that the interactions are modelled using a realistic many-body potential such as EMT, the Embedded Atom Method (Daw and Baskes 1984) or the Finnis-Sinclair model (Finnis and Sinclair 1984, 1986). Pair potentials such as Lennard-Jones are still seen used for simulating metals due to the lower computational burden.\textsuperscript{1} Although they give a good description of noble gas solid, they are not adequate for modelling the bonding in metallic systems. One symptom of this is seen in the elastic constants, all pair potentials result in materials that satisfies the Cauchy relations between the elastic constants ($C_{12} = C_{44}$ for cubic crystals), a relation that is far from true in most metals.

In the simulations, the samples are deformed by slowly increasing the system size along the $z$ axis while minimising the energy with respect to all atomic coordinates and with respect to the box dimensions in the $x$ and $y$ directions. The minimisation is done as a modified molecular

\textsuperscript{1}Typically, many-body potentials require approximately ten times as much computer power as Lennard-Jones potentials.
Simulations of mechanics and structure of nanomaterials — from nanoscale to coarser scales

Fig. 2: Stress-strain curves for eight simulations with four different grain sizes $d$. A total of 28 simulations were performed, but for clarity only eight are shown here. The fluctuations in the individual curves and the differences between curves at the same grain size, are due to the low number of grains in each system.

dynamics simulation. After each timestep the dot product between the momentum and the force is calculated for each atom. Any atom where the dot product is negative gets its momentum zeroed, as it is moving in a direction where the potential energy is increasing. This $MDmin$ algorithm (Stoltze 1997) is very efficient for this type of minimisation. Before each timestep, the system is stretched a little along the $z$ direction. The two lateral dimensions are optimised by a Monte Carlo procedure: every 20 timesteps a change in the dimensions is proposed, if the change results in a lower energy it is accepted, otherwise it is discarded. A few simulations were performed using the conjugate gradient algorithm for energy minimisation (Press, Flannery, Teukolsky and Vetterling 1988). The two algorithms were approximately equally efficient.

2.3. Analysis. During the simulation, the local stresses were calculated and stored for further analysis, and the global values of the stress tensor were stored to generate stress-strain curves. A set of stress-strain curves is shown in Fig. 2.

To facilitate the analysis of the simulations, the local order in the sample was analysed. This was done using a method called Common Neighbour Analysis (Jónsson and Andersen 1988; Clark and Jónsson 1993). By investigating the bonds between the neighbouring atoms to the atom under investigation, the local crystal structure is determined. Atoms are then classified into three classes. Atoms in a local f.c.c. order are considered ordinary bulk atoms; atoms in local h.c.p. order are labelled as belonging to a stacking fault or the like; and atoms in all other local orders are considered part of the grain boundaries or of dislocation cores. This classification can be seen in Fig. 1.

2.4. Results. Fig. 3a shows the average stress-strain curves at each grain size. A clear grain size dependence is seen in the maximal flow stress. Fig. 3b and c summarise the results, showing the maximal flow stress and the 0.2% offset yield stress in a standard Hall-Petch plot, i.e. as a function of one over the square root of the grain size. A reverse Hall-Petch effect is clearly seen, it will be
In Fig. 1b stacking faults are present in several grains. They are created as partial dislocations (Shockley partials) move through the grains. They would be removed if a second partial dislocation followed in the same plane. This is, however, rarely seen, possibly because the grain size is comparable to the splitting width of the dislocation. Simulations of dislocation emission from a notch in a surface (Schiøtz, Jacobsen and Nielsen 1995) have shown that the leading partial will move several splitting widths away from the notch, before the trailing partial is emitted. Possibly a similar effect is seen here.

We have measured the amount of dislocation activity in the systems. The total dislocation activity is able to explain at most 2–3% plastic deformation, i.e. less than half the observed plastic deformation. To identify the nature of the remaining deformation, we analysed the relative motion of the individual atoms. Fig. 4a shows the magnitude of the motion of the atoms obtained by subtracting the coordinates at two different strains (differing by 0.4%). The collective motion due to the imposed strain rate has been subtracted out. Darker atoms move most. By comparing with Fig. 4b showing the positions of the grain boundaries, it is seen that the motion occurs mainly in the grain boundaries. An indication of the activity in the grain boundaries can also be seen in
Simulations of mechanics and structure of nanomaterials — from nanoscale to coarser scales

Fig. 4: (a) The relative motion of the atoms in the $z$ direction (up in the plane of the paper) during the preceding 0.4% deformation. Darker atoms move more than light atoms. We see many small, independent slip events in the grain boundaries, this is the main deformation mode. (b) The position of the grain boundaries and stacking faults at this point in the simulation. Adapted from Schiøtz et al. (1998).

Fig. [3]: the grain boundaries have become a little thicker during deformation.

3. THE REVERSE HALL-PETCH EFFECT

As is seen in Fig. [3], a reverse Hall-Petch effect is observed in the simulations, i.e. the material gets softer as the grain size is decreased. This is opposite of the normally seen behaviour, but has occasionally been observed experimentally in nanocrystalline materials with sufficiently small grain sizes (Chokshi, Rosen, Karch, Gleiter 1989). There are also observations of “kinked” Hall-Petch graphs, i.e. cases where the slope is reduced (but still positive) below a certain grain size. Many explanations have been proposed, of which some are summarised below. The explanations are not necessarily mutually exclusive, nor is it unlikely that different explanations may apply depending on the way the material was produced. It seems reasonable to assume that the deformation mechanism is different in samples produced by e.g. inert gas condensation, producing essentially dislocation-free grains, and by severe plastic deformation, where the small grains are produced by breaking up larger grains through intense dislocation activity. The most commonly proposed explanations are increased diffusional creep, suppression of dislocation pileups, different grain boundary structures, poor sample quality (porosity and other flaws), and deformation in the grain boundaries.

3.1. Enhanced Coble creep. Chokshi et al. (1989) propose that the reverse Hall-Petch effect is caused by enhanced Coble creep, i.e. creep due to diffusion in the grain boundaries. Coble creep scales with the grain size ($d$) as $d^{-3}$, and estimates of the creep rate of nanocrystalline metals indicate that this could be the explanation of the reverse Hall-Petch effect. Direct measurements
of the creep rate have, however, ruled out this explanation (Nieman, Weertman and Siegel 1990; Nieh and Wadsworth 1991).

3.2. Suppression of dislocation pileups. The Hall-Petch effect is normally explained by appealing to dislocation pileups near the grain boundaries. Once the grain size drops below the equilibrium distance between dislocations in a pileup, pileups are no longer possible, and the Hall-Petch relation should cease to be valid (Nieh and Wadsworth 1991; Pande, Masumura and Armstrong 1993). It is, however, not clear how the yield stress should depend on the grain size below that point. The critical grain size is estimated to be 20 nm for copper (Nieh and Wadsworth 1991).

3.3. Different grain boundary structures. It is not unreasonable to assume that the grain boundary structure might be different when the grain size is very small (Zhu, Birringer, Herr and Gleiter, 1987). It has been proposed that grain boundaries in nanocrystalline metals may be more "transparent" to dislocations, and thus allow dislocations to run through several grains (Valiev, Chmelik, Bordeaux, Kapelski and Baudelet 1992; Lian, Baudelet and Nazarov 1993; Lu and Sui 1993). This was proposed in connection with measurements of a possible breakdown of the Hall-Petch relation in metals with sub-micrometer grain sizes, produced by severe plastic deformation (Valiev et al. 1992). Recent high-resolution electron microscopy studies show, that the grain boundaries in metals produced in this way have a complex structure, with a large number of dislocations very close to the grain boundary (Horita, Smith, Furukawa, Nemoto, Valiev and Langdon 1996). This should make the grain boundaries less transparent to dislocations, but a change in slope in the Hall-Petch relation is seen at grain sizes below 100 nm (Furukawa, Horita, Nemoto, Valiev and Langdon 1996). They explain the change as enhanced plasticity due to these extra dislocations near the grain boundaries.

3.4. Porosity and flaws. Many of the observations of a reverse Hall-Petch effect are from samples generated using inert gas condensation, where a large number of nanometer-sized clusters are compacted to produce the sample. If the compaction is not complete, small voids will be present between the grains. The presence of these voids was not initially recognised, the lower density being ascribed to special low-density grain boundaries. If the nanocrystalline metal contains a significant volume fraction of porosity, this will obviously reduce the hardness significantly. Surface defects alone have been shown to be able to reduce the strength of nanocrystalline metals by a factor of five (Nieman, Weertman and Siegel 1991; Weertman 1993).

Many of the early measurements of a reverse Hall-Petch effect are likely to have been caused by unrecognised porosity in the samples. Improved techniques (Sanders, Fougere, Thompson, Eastman and Weertman 1997) have allowed production of nanocrystalline samples with densities above 98%, these have shown no reverse Hall-Petch effect in copper at grain sizes down to approximately 10–15 nm (Sanders, Youngdahl and Weertman 1997).

3.5. Deformation in the grain boundaries. As the grain size is reduced, the volume fraction of the grain boundaries increase, and it is reasonable to assume that at some point they will begin to play a role in the deformation process. Li, Sun and Wang (1994) propose a deformation mechanism based on motion of grain boundary dislocations.
Simulations of mechanics and structure of nanomaterials — from nanoscale to coarser scales

Fig. 5: Stress stress curves for simulations at room temperature. Each curve shows the average over four simulations. The simulations were done using constant-energy molecular dynamics at a strain rate of $5 \cdot 10^8 \text{s}^{-1}$. $d$ is the grain size.

3.6. The role of computer simulations. Computer simulations give a possibility to distinguish between this large number of different explanations. The computer simulations presented here clearly indicate that a new deformation mechanism becomes active in the grain boundaries (Schiøtz et al. 1998). It does not appear to be a grain boundary dislocation based motion, but rather a large number of small events, where only a few atoms (or a few tens of atoms) move simultaneously (Fig. 4). This produces a large number of small, apparently uncorrelated slipping events in the grain boundaries, leading to grain boundary sliding. The processes also lead to the grain boundaries becoming thicker (Fig. 1). This does, however, seem to be a result of doing the simulations at zero temperature. Simulations at room temperature do not result in a change in the grain boundary thickness, otherwise the results are very similar apart from a reduction of the yield and flow stresses due to increased grain boundary sliding (Fig. 5).

Simulations of nanocrystalline nickel also show that the main deformation mechanism is grain boundary sliding and grain boundary motion, where one grain grows at the expense of another (Van Swygenhoven and Caro, 1997a,b). Those simulations are stress controlled, i.e. the stress is controlled, and the strain is measured, contrary to the simulations reported here, which are strain controlled. The strain rate was measured as a function of grain size, giving a higher strain rate at lower grain boundaries, consistent with a viscoelastic behaviour of the grain boundaries (Van Swygenhoven and Caro, 1997b).

Simulations of the sintering of nanocrystalline Cu particles to form a fully dense nanocrystalline sample also indicate that the main deformation is in the grain boundaries (Zhu and Averback, 1996).

The observations of a reverse Hall-Petch effect in the simulations presented here are not in conflict with the experiments reported by Sanders et al. (1997), since the experiments were done on samples with grain sizes above 10–15 nm. In order to investigate if the transition between the normal and the reverse Hall-Petch effect could be observed, a version of the simulation program

9
was written for parallel computers. This allowed us to increase the number of atoms by a factor of ten, thus more than doubling the grain size. Such a simulation is shown in Fig. 6. Preliminary results indicate that the reverse Hall-Petch effect persists at these grain sizes.

4. BEYOND THE ATOMIC SCALE

As larger systems are being considered, atomic scale simulations quickly become impossible: doubling the characteristic length scale typically means increasing the volume, and thus the number of atoms, by a factor eight. At present, simulations with up to 100 million atoms are possible using parallel supercomputers (Abraham 1997; Abraham et al. 1997; Zhou et al. 1997), corresponding to a system of less than 100 nm cubed. If a larger system is to be studied, simulations
Simulations of mechanics and structure of nanomaterials — from nanoscale to coarser scales

which consider individual atoms cannot in practise be carried out. In this section we give a short
summary over a few methods that go beyond an atomic description to describe the material at
a coarser length scale. See also the review by Carlsson and Thomson (1998), where simula-
tion techniques at different length scales are discussed in the context of how to calculate fracture
toughness.

4.1. Simulations based on individual dislocations. The idea behind “dislocation dynamics” is to
use individual dislocations as “fundamental particles” in the simulations, i.e. to describe the mate-
rial as consisting of a collections of dislocations that interact with each other through their elastic
fields. This is a sensible idea when studying properties dominated by the dislocation dynamics, but
cannot be expected to work without modifications in cases where other defect types (e.g. cracks
and grain boundaries) play a significant role.

In principle the methods developed for atomistic simulations can be used, provided one replaces
the interatomic interactions with the formula for interactions between dislocations. There are,
however, a number of complications:

1. Dislocations are lines, not points, i.e. the position of a dislocation cannot be described by a
single set of coordinates.

2. Both the force acting between dislocations, and the equation of motion for a single disloca-
tion are highly anisotropic.

3. Interactions between dislocations are long ranged, the force decays as \(1/r\), whereas the
forces between atoms in a metal decay exponentially due to screening effects. It is thus not
possible to introduce a cutoff distance beyond which dislocations do not interact. Attempts
to introduce such cutoffs have been shown to cause the emergence of spurious structures
with a characteristic length scale equal to the chosen cutoff (Gulluoglu, Srolovitz, LeSar
and Lomdahl 1989; Holt 1970).

4. Although the long-range elastic forces between dislocations are well known, the parameters
describing the short-range interactions (dislocation crossing, cross slip, annihilation etc.)
are presently not well known, and will have to be extracted from experiments, come from
theoretical arguments or come from atomic-scale simulations.

Barts and Carlsson (1995) have developed a method for simulating the interactions of a large
number of dislocations in two-dimensional systems. In two dimensions the dislocations are
points, eliminating the first problem mentioned above, and simplifying the interactions signifi-
cantly. The drawback is of course that the simulations are limited to problems that are essentially
two-dimensional, i.e. where the dislocations are parallel and straight. One such problem, which
has been successfully modelled, is polygonisation in single glide (Barts and Carlsson 1997). They
solve the problem of the long range interactions between dislocations by using a Fourier transform
of the long range part of the interactions, resulting in a method where the required computer time
scales linearly with the number of dislocations.
Similar methods can be developed in three dimensions, as demonstrated by Kubin and coworkers (Kubin, Canova, Condat, Devincre, Pontikis and Bréchet 1992; Devincre and Kubin 1997). They solve the problem of representing the position of the dislocation strings by modelling the dislocations as consisting of a chain of straight segments of pure screw or edge dislocations, where each segment can be oriented along a finite number of directions. The interactions between the dislocations are then described by the interactions of the individual segments. The method has been used to study the influence of cross slip on work hardening (Devincre and Kubin 1994) and on pattern formation during cyclic deformation (Kratochvíl, Saxlová, Devincre and Kubin 1997).

4.2. Simulations based on dislocation densities. When the structures under consideration become larger, even dislocation based simulations become unwieldy. It is tempting to attempt to make a model based on a continuum description of the dislocation density, i.e. by replacing the positions of individual dislocations by a continuous dislocation density. A simple scalar density is clearly insufficient to describe the dislocations; as a dislocation is described by two vectors (the sense and the Burgers vector), the density becomes a tensor (Nabarro 1987).

As shown by Barts and Carlsson (1997) a continuum description based on the dislocation density tensor alone is insufficient to describe a relatively simple patterning process such as polygonisation. This is because the stress field from a dislocation wall is caused by the discrete dislocation positions, and vanish in a continuum model. They propose that a continuum model should contain additional variables describing the local environment of the dislocations. It is at present unclear if such a description can be made.

For an overview of the work that has been done on continuum modelling of dislocations, see the review by Selitser and Morris (1994).

4.3. Simulations based on grains. For some types of simulations, an even coarser length scale can be used: the scale set by the size of the grains. In typical metals this will be of the order of 100 µm. At this length scale one may consider the grains as the fundamental unit of the simulation. This approach has successfully been used e.g. to study recrystallization and the evolution of texture during growth (Juul Jensen 1997a,b and references therein).

4.4. Finite-element methods. For engineering purposes, the relevant length scale will be set by the physical dimensions of the sample. Typically simulations ignore the grain structure of the material, which is treated as homogeneous (but possibly anisotropic). A continuum description based on the stress and strain fields is used, and the field equations are typically solved using finite element methods.

5. BRIDGING THE LENGTH SCALES

To gain a fuller understanding of material properties, modelling at several length scales should be combined (often referred to as “multiscale modelling”). Typically, experiments or simulations at one length scale suggests interesting phenomena to study at a shorter length scale, the result of which is used as parameters in models at a longer length scale. In the following we will give
Simulations of mechanics and structure of nanomaterials — from nanoscale to coarser scales

some examples, followed by some examples of “hybrid” simulation techniques, where several simulation paradigms are combined in a single simulation.

5.1. Interactions between simulations at different length scales. Dislocation level simulations require the knowledge of details of the short-range interactions between dislocations. Many of these can come from atomic-scale simulations. This can be done by setting up a very large system, and observe the dislocation processes in this system. Bulatov et al. (1998) have studied the behaviour of the cloud of dislocations emitted from a crack in an f.c.c. metal, and observed the creation and subsequent destruction of a Lomer-Cotrell lock. They propose to extract parameters for dislocation level simulations from such atomistic simulations. Schiøtz, Jacobsen, and Nielsen (1995) have observed a new dislocation multiplication mechanism that may be active under extremely large strain rates.

If the main goal of the simulation is to provide knowledge of a specific dislocation process, a more specialised simulation setup may be advantageous. Zhou, Preston, Lomdahl and Beazley (1998) have simulated the formation of a jog through the intersection of two extended dislocations. The simulations show the details of the interaction and provides an estimate of the involved critical stresses.

Recently an advanced simulation technique, the “Nudged Elastic Band (NEB) Method” (Mills, Jónsson and Schenter 1995) was used to study cross slip of screw dislocations at the atomic scale (Rasmussen, Jacobsen, Leffers, Pedersen, Srinivasan and Jónsson 1997; Pedersen, Carstensen and Rasmussen 1998). The NEB method identifies the entire transition path and can thus be used to find the energy of the transition state. This makes the method very suitable for studying elementary dislocation reactions, and can provide good input for dislocation level simulations. The group is presently using the technique to study dislocation annihilation (Pedersen et al. 1998).

5.2. Hybrid simulation techniques. A number of simulation techniques have been developed, where several simulation techniques are combined in a “hybrid” simulation. Typically, the idea is to describe “interesting” parts of the simulation atomistically, while other parts of the system are described by a model based on linear elasticity theory. The rationale behind this is that in most large-scale simulations, the majority of the atoms do not participate actively in the processes being studied, their main role is to propagate the elastic fields. In these regions of the simulation the strains are typically small, and linear elasticity is a good description. At the same time an atomistic description is required in dislocation core and other parts of the system, where non-linearities play a role.

The simplest way of doing this is by dividing the simulations into two zones. In the inner zone an atomistic description is used. The inner zone is surrounded by a much larger outer zone, described by elasticity theory typically using a continuous finite element method (Kohlhoff, Gumbsch and Fishmeister 1991; Gumbsch 1995). In this way the long-range elastic field is described in a computationally inexpensive way, and the atoms in the atomistic region see the correct response from the surrounding material. Great care must be taken in matching the two regions.
A related method consists of using a lattice Green’s function to describe the linear region (Thomson, Zhou, Carlsson, and Tewary 1992; Canel, Carlsson, and Thomson 1995; Schiøtz and Carlsson 1997). In this method the atoms in the outer zone are considered to interact through linear spring forces, and the force matrix is inverted giving a lattice Green’s function. The Green’s function thus describes the displacement of the lattice at one point resulting from a force acting on the lattice at another point. The degrees of freedom associated with the atoms in the outer zone (typically a few million atoms) can then be eliminated, and only the degrees of freedom associated with the atoms in the inner zone need to be retained (typically less than 1000), together with the elements of the Green’s function matrix connecting atoms in the inner zone. The method has been used to study dislocation emission from sharp and blunt cracks (Zhou, Carlsson, and Thomson 1993, 1994; Schiøtz, Canel, and Carlsson 1997). A similar technique was used by Rao, Hernandez, Simmons, Parthasarathy, and Woodward (1998) to study dislocation core structures.

The above-mentioned techniques have the disadvantage that the system must a priori be divided into two “zones”, and dislocations and cracks are confined to the inner zone. An adaptive technique has been developed (Tadmor, Ortiz and Phillips 1996; Shenoy, Miller, Tadmor, Rodney, Phillips, and Ortiz, to be published). In this method the system is described by a finite element method, but instead of an ordinary constitutive relation, the energy is calculated from a tiny atomistic simulation. Where necessary, the finite element mesh is automatically refined, eventually continuing until it is so fine that each element only contains one atom. In this limit the simulation converges to an ordinary atomistic simulation. The method is adaptive, so the mesh is automatically refined in areas where a detailed description is required, and coarsened where less detail is required. The method has been used to study the interactions of dislocations and cracks with grain boundaries (Shenoy, Miller, Tadmor, Phillips, and Ortiz 1998; Shenoy et al., to be published).

6. CONCLUSIONS

We have demonstrated how atomic-scale simulations can be used to obtain information about the deformation mechanisms in nanocrystalline metals. We find that at these grain sizes the dominating deformation mechanism is sliding in the grain boundaries through a large number of small events in the grain boundary. Each event only involves a few atoms. The result of this large number of small events is a flow in the grain boundaries, permitting the grains to slide past each other with only a minor amount of deformation inside the grains. The deformation mechanism results in a reverse Hall-Petch effect, where the material becomes softer when the grain size is reduced. This is caused by an increase of fraction of the atoms that are in the grain boundaries as the grain size is reduced. We have not yet been able to observe the cross-over between the range of grain sizes where this deformation mechanism dominates, and grain sizes where a conventional deformation mechanism based on dislocation motion dominates. The hardness and yield stress of nanocrystalline metals is expected to reach its maximum in this cross-over region.

In order to simulate larger systems than the ones considered here, the atomic-scale approach must be abandoned. We have provided an overview of simulation techniques at coarser scales, and have indicated how they can be combined with atomic-scale simulations to provide models of the mechanics of metals at multiple length scales. These techniques have not yet become mainstream
Simulations of mechanics and structure of nanomaterials — from nanoscale to coarser scales

simulation tools, but it is likely that many of them will gain more widespread usage in the near future.

7. ACKNOWLEDGMENTS

Center for Atomic-scale Materials Physics is sponsored by the Danish National Research Council. The present work was in part financed by The Danish Technical Research Council through Grant No. 9601119. Parallel computer time was financed by the Danish Research Councils through Grant No. 9501775.

REFERENCES

Abraham, F. F. (1997). On the transition from brittle to plastic failure in breaking a nanocrystal under tension (NUT). Europhys. Lett. 38, 103–106.

Abraham, F. F., Schneider, D., Land, B., Lifka, D., Skovira, J., Gerner, J., and Rosenkrantz, M. (1997). Instability dynamics in three-dimensional fracture: an atomistic simulation. J. Mech. Phys. Solids 45, 1461–1471.

Barts, D. B. and Carlsson, A. E. (1995). Order-N method for force calculation in many-dislocation systems. Phys. Rev. E 52, 3195.

Barts, D. B. and Carlsson, A. E. (1997). Simulation and theory of polygonization in single glide. Phil. Mag. A 75, 541–562.

Bulatov, V., Abraham, F. F., Kubin, L., Devincre, B., and Yip, S. (1998). Connecting atomistic and mesoscale simulations of crystal plasticity. Nature 391, 669–672.

Canel, L. M., Carlsson, A. E., and Thomson, R. (1995). Efficient effective-energy method for lattice-Green’s-function simulations of fracture. Phys. Rev. B 52, 158–167.

Carlsson, A. E. and Thomson, R. (1998). Fracture toughness of materials: From atomistics to continuum theory. Solid State Physics 51, 233–280.

Chen, D. (1995). Structural modeling of nanocrystalline materials. Comput. Mater. Sci. 3, 327–333.

Chokshi, A. H., Rosen, A., Karch, J., and Gleiter, H. (1989). On the validity of the Hall-Petch relationship in nanocrystalline materials. Scripta Metall. 23, 1679–1684.

Clarke, A. S. and Jónsson, H. (1993). Structural changes accompanying densification of random-sphere packings. Phys. Rev. E 47, 3975–3984.

D’Agostino, G. and Van Swygenhoven, H. (1996). Structural and mechanical properties of a simulated nickel nanophase. Mat. Res. Soc. Symp. Proc. 400, 293–298.

Daw, M. S. and Baskes, M. I. (1984). Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals. Phys. Rev. B 29, 6443–6453.

Devincre, B. and Kubin, L. P. (1994). Three dimensional simulations of plasticity. In: Strength of Materials, edited by H. Oikawa, K. Maruyama, S. Takeuchi, and M. Yamaguchi (The Japan Institute of Metals). pp. 179–182.

Devincre, B. and Kubin, L. P. (1997). Mesoscopic simulations of dislocations and plasticity. Mater. Sci. Eng. A 234-236, 8–14.

Finnis, M. W. and Sinclair, J. E. (1984). A simple empirical N-body potential for transition metals. Phil. Mag. A 50, 45–55.
Schiøtz, Vegge, Di Tolla and Jacobsen

Finnis, M. W. and Sinclair, J. E. (1986). Erratum. Phil. Mag. A 53, 161.

Furukawa, M., Horita, Z., Nemoto, M., Valiev, R. Z., and Langdon, T. G. (1996). Microhardness measurements and the Hall-Petch relationship in an Al–Mg alloy with submicrometer grain size. Acta Mater. 44, 4619–4629.

Gulluoglu, A. N., Srolovitz, D. J., LeSar, R., and Lomdahl, P. S. (1989). Dislocation distributions in two dimensions. Scr. Met. 23, 1347–1352.

Gumbsch, P. (1995). An atomistic study of brittle fracture: Toward explicit failure criteria from atomistic modeling. J. Mater. Res. 10, 2897–2907.

Hall, E. O. (1951). The deformation and ageing of mild steel: III Discussion of results. Proc. Phys. Soc. London B 64, 747–753.

Holt, D. L. (1970). Dislocation cell formation in metals. J. Appl. Phys. 41, 3197–3201.

Horita, Z., Smith, D. J., Furukawa, M., Nemoto, M., Valiev, R. Z., and Langdon, T. G. (1996). An investigation of grain boundaries in submicrometer-grained Al–Mg solid solution alloys using high-resolution electron microscopy. J. Mater. Res. 11, 1880–1890.

Jacobsen, K. W., Nørskov, J. K., and Puska, M. J. (1987). Interatomic interactions in the effective-medium theory. Phys. Rev. B 35, 7423–7442.

Jacobsen, K. W., Stoltze, P., and Nørskov, J. K. (1996). A semi-empirical effective medium theory for metals and alloys. Surf. Sci. 366, 394–402.

Jónsson, H. and Andersen, H. C. (1988). Icosahedral ordering in the Lennard-Jones liquid and glass. Phys. Rev. Lett. 60, 2295–2298.

Juul Jensen, D. (1997a). Orientational Aspects of Growth during Recrystallization (Risø, Roskilde).

Juul Jensen, D. (1997b). Simulation of recrystallization microstructures and textures: Effects of preferential growth. Metall. Mater. Trans. A 28A, 15–25.

Kohlhoff, S., Gumbsch, P., and Fischmeister, H. F. (1991). Crack propagation in b.c.c. crystals studied with a combined finite-element and atomistic model. Phil. Mag. A 64, 851–878.

Kratochvíl, J., Saxlová, M., Devincre, B., and Kubin, L. P. (1997). On the sweeping of dipolar loops by gliding dislocations. Mater. Sci. Eng. A 234-236, 318–321.

Kubin, L. P., Canova, G., Condat, M., Devincre, B., Pontikis, V., and Bréchet, Y. (1992). Dislocation microstructures and plastic flow: a 3D simulation. Solid State Phenomena 23–24, 455–472.

Li, S., Sun, L., and Wang, Z. (1994). A grain boundary model of Hall-Petch relationship in nanocrystalline materials. In: Strength of Materials, edited by H. Oikawa, K. Maruyama, S. Takeuchi, and M. Yamaguchi (The Japan Institute of Metals), pp. 873–876, pp. 873–876.

Lian, J., Baudelet, B., and Nazarov, A. A. (1993). Model for the prediction of the mechanical behaviour of nanocrystalline materials. Mater. Sci. Eng. A 172, 23–29.

Lu, K. and Sui, M. L. (1993). An explanation to the abnormal Hall-Petch relation in nanocrystalline materials. Scripta Metall. Mater. 28, 1465–1470.

Mills, G., Jönsson, H., and Schenter, G. K. (1995). Reversible work transition state theory: application to dissociative adsorption of hydrogen. Surf. Sci. 324, 305–337.

Morris, D. G. and Morris, M. A. (1997). Hardness, strength, ductility and toughness of nanocrystalline materials. Mater. Sci. Forum 235-238, 861–872.

Nabarro, F. R. N. (1987). Theory of crystal dislocations (Dover, New York).

Nieh, T. G. and Wadsworth, J. (1991). Hall-Petch relation in nanocrystalline solids. Scripta Met. Mater. 25, 955–958.
Simulations of mechanics and structure of nanomaterials — from nanoscale to coarser scales

Nieman, G. W., Weertman, J. R., and Siegel, R. W. (1990). Tensile strength and creep properties of nanocrystalline palladium. Scripta Met. Mater. 24, 145–150.

Nieman, G. W., Weertman, J. R., and Siegel, R. W. (1991). Mechanical behavior of nanocrystalline Cu and Pd. J. Mater. Res. 6, 1012–1027.

Pande, C. S., Masumura, R. A., and Armstrong, R. W. (1993). Pile-up based Hall-Petch relation for nanoscale materials. Nanostruct. Mater. 2, 323–331.

Pedersen, O. B., Carstensen, J. V., and Rasmussen, T. (1998) These proceedings.

Petch, N. J. (1953). The cleavage strength of polycrystals. J. Iron Steel Inst. 174, 25.

Phillpot, S. R., Wolf, D., and Gleiter, H. (1995a). Molecular-dynamics study of the synthesis and characterization of a fully dense, three-dimensional nanocrystalline material. J. Appl. Phys. 78, 847–860.

Phillpot, S. R., Wolf, D., and Gleiter, H. (1995b). A structural model for grain boundaries in nanocrystalline materials. Scripta Met. Mater. 33, 1245–1251.

Press, W. H., Flannery, B. P., Teukolsky, S. A., and Vetterling, W. T. (1988). Numerical recipes in C (Cambridge University Press, Cambridge).

Rao, S., Hernandez, C., Simmons, J. P., Parthasarathy, T. A., and Woodward, C. (1998). Green’s function boundary conditions in two-dimensional and three-dimensional atomistic simulations of dislocations. Phil. Mag. A 77, 231–256.

Rasmussen, T., Jacobsen, K. W., Jeffers, T., Pedersen, O. B., Srinivasan, S. G., and Jonsson, H. (1997). Atomistic determination of cross-slip pathway and energetics. Phys. Rev. Lett. 79, 3676–3679.

Sanders, P. G., Fougere, G. E., Thompson, L. J., Eastman, J. A., and Weertman, J. R. (1997a). Improvements in the synthesis and compaction of nanocrystalline materials. Nanostruct. Mater. 8, 243–252.

Sanders, P. G., Youngdahl, C. J., and Weertman, J. R. (1997b). The strength of nanocrystalline metals with and without flaws. Mater. Sci. Eng. A 234–236, 77–82.

Schiotz, J., Canel, L. M., and Carlsson, A. E. (1997). Effects of crack tip geometry on dislocation emission and cleavage: A possible path to enhanced ductility. Phys. Rev. B 55, 6211–6221.

Schiotz, J. and Carlsson, A. E. (1997). Calculation of elastic Green’s functions for lattices with cavities. Phys. Rev. B 56, 2292–2294. (BR).

Schiotz, J., Di Tolla, F. D., and Jacobsen, K. W. (1998). Softening of nanocrystalline metals at very small grain sizes. Nature 391, 561–563.

Schiotz, J., Jacobsen, K. W., and Nielsen, O. H. (1995). Kinematic generation of dislocations. Phil. Mag. Lett. 72, 245–250.

Selitser, S. I. and Morris, J. W. (1994). Substructure formation during plastic deformation. Acta Metall. Mater. 42, 3985–3991.

Shenoy, V. B., Miller, R., Tadmor, E. B., Phillips, R., and Ortiz, M. (1998). Quasicontinuum models of interfacial structure and deformation. Phys. Rev. Lett. 80, 742–745.

Shenoy, V. B., Miller, R., Tadmor, E. B., Rodney, D., Phillips, R., and Ortiz, M. (to be published). An adaptive finite element approach to atomic-scale mechanics — the quasicontinuum method (preprint cond-mat/9710027).

Siegel, R. W. and Fougere, G. E. (1994). Mechanical properties of nanophase materials. In: Nanophase Materials: Synthesis — Properties — Applications, edited by G. C. Hadjipanayis and R. W. Siegel (Kluwer, Dordrecht), vol. 260 of NATO-ASI Series E: Applied Sciences, pp.
Stoltze, P. (1997). Simulation methods in atomic scale materials physics (Polyteknisk Forlag, Lyngby, Denmark).

Tadmor, E. B., Ortiz, M., and Phillips, R. (1996). Quasicontinuum analysis of defects in solids. Phil. Mag. A 73, 1529–1564.

Thomson, R., Zhou, S. J., Carlsson, A. E., and Tewary, V. K. (1992). Lattice imperfections studied by the use of lattice Green’s functions. Phys. Rev. B 46, 10613–10622.

Valiev, R. Z., Chmelik, F., Bordeaux, F., Kapelski, G., and Baudelet, B. (1992). The Hall-Petch relation in submicron-grained Al-1.5%Mg alloy. Scripta Metall. Mater. 27, 855–860.

Van Swygenhoven, H. and Caro, A. (1997a). Molecular dynamics computer simulation of nanophase Ni: structure and mechanical properties. Nanostructured Materials 9, 669–672.

Van Swygenhoven, H. and Caro, A. (1997b). Plastic behavior of nanophase Ni: a molecular dynamics computer simulation. Appl. Phys. Lett. 71, 1652–1654.

Weertman, J. R. (1993). Hall-Petch strengthening in nanocrystalline metals. Mater. Sci. Eng. A 166, 161–167.

Zhou, S. J., Beazley, D. M., Lomdahl, P. S., and Holian, B. L. (1997). Large-scale molecular dynamics simulations of three-dimensional ductile failure. Phys. Rev. Lett. 78, 479–482.

Zhou, S. J., Carlsson, A. E., and Thomson, R. (1993). Dislocation nucleation and crack stability: Lattice Green’s-function treatment of cracks in a model hexagonal lattice. Phys. Rev. B 47, 7710–7719.

Zhou, S. J., Carlsson, A. E., and Thomson, R. (1994). Crack blunting effects on dislocation emission from cracks. Phys. Rev. Lett. 72, 852–855.

Zhou, S. J., Preston, D. L., Lomdahl, P. S., and Beazley, D. M. (1998). Large-scale molecular dynamics simulation of dislocation intersection in copper. Science 279, 1525–1527.

Zhu, H. and Averback, R. S. (1996). Sintering of nano-particle powders: simulations and experiments. Materials and Manufacturing Processes 11, 905–923.

Zhu, X., Birringer, R., Herr, U., and Gleiter, H. (1987). X-ray diffraction studies of nanometer-sized crystalline materials. Phys. Rev. B 35, 9085–9090.