COMPUTATIONAL APPROACHES TO NANOMINERALOGY

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INTRODUCTION

Nanomineralogy is concerned with the behavior of minerals on length scales between 10 Å and 1 micron. Within the realm of computational science, molecular modeling methods have been working at the lower end of this scale for more than 50 years and comprise a relatively mature field even within the geosciences community (see Cygan and Kubicki, 2001). Somewhere near the upper end of this scale, continuum approaches using bulk thermodynamics and homogeneous transport properties (diffusion, viscous flow and heat flow, and elastic moduli) can be used effectively (Turcotte and Schubert, 1982). From one perspective, the nanoscale regime is the theoretical/computational no-man’s land between atomistic and continuum scales, in which atoms cannot quite be ignored and continuum models cannot quite be applied. More generally, it is the simultaneous consideration of multiple scales, each requiring different methods, which, from the computational point of view, provides the driving force and makes this field exciting. The focus of this volume is on nanoscale phenomena in mineralogy and geochemistry in low-temperature, near-surface environments. This is indeed a rich area for multiscale investigations, as shown in Figure 1. At the finest scales, one is interested in the spatio-temporal variability of the collective wave functions (or density) of electrons. At a simple level, this results in the formation of chemical bonds. Even at this scale, consideration of the detailed aspects of electron density topology is an emerging area (Bader, 1990; Gibbs et al., 1998; Rescigno et al., 1999; Blanco et al., 2000; Espinosa and Molins, 2000). As more than a few atoms begin to interact, complexity begins to be revealed in molecular arrangements as well as the electronic structure. In mineralogy, we have the polynuclear clusters (such as discussed in detail by Casey and Furrer in this volume) and nanoporous minerals, such as cacoxenite and zeolites (Gier and Stucky, 1991; Patarin and Kessler, 2000). In materials science and chemistry, we have the familiar nanotubes (Mintmire and White, 1998) and buckyballs (Lof et al., 1992). The field of supramolecular chemistry also operates in this regime and is concerned with controlled assembly of these building blocks into chemical machines (Varnek et al., 2000). These polynuclear molecules also form building blocks for familiar oxide minerals (Schwertmann et al., 1999; Cannas et al., 2001; Casey and Furrer, this volume). The process of assembly of these molecules leads to the elaborate crystal shapes and distributions familiar in nonequilibrium low-temperature aqueous environments (Dixon and Weed, 1989). Familiar heterogeneities at this scale include surfaces with terraces and kinks, dislocations, and grain boundaries, including aqueous mineral interfaces. At still larger scales, we have heterogeneities associated with agglomerating mineral assemblages and other forms of phase separation, such as exsolution phenomena. Agglomeration in itself is a multiscale process that, at very small scales, plays an
important role in the assembly of single oxide crystals (Banfield et al., 2000; Penn et al., 2001a). At larger scales, this leads us to the pore-scale regime of concern in reactive transport investigations (Yabusaki et al., 2001).

Computational methods capable of spanning these scales take two types of approaches. The more familiar is the serial approach. For example, electronic structural calculations on small systems are used to parameterize tight binding or classical potential functions. Molecular dynamics (MD) or Monte Carlo methods are applied to the potential functions to obtain transport phenomena or thermodynamic quantities. In some cases, transport coefficients derived in this way are used in continuum models at the next level. Systems with moving inhomogeneities, such as crack propagation, or highly collective problems having complex structural characteristics often require a multiresolution approach that combines simultaneously continuum, atomistic, and electronic structural components (Broughton, 1999). In such systems, it is often not possible to isolate scales and eliminate them through averaging or through parameterization. Even before doing any physicochemical modeling, just specifying the initial conditions in an inherently multiscale system is a challenging task. The multiresolution aspects are as important in time as in space (if not more so).

What motivation exists for building a multiscale understanding of mineralogical systems? For the geoscientist interested in near-surface environments, probably the most compelling reason to study these multiscale phenomena from a simulation perspective is to sort out the various factors contributing to chemical reactivity in terms of both energetics and rates. The sorption of chromate, or even the uptake of protons in these morphologically intricate minerals, involves highly coupled contributions from electronic structure, surface topography, and long-range viscoelastic and solvent effects. For example, even something as fundamental as the point of zero charge of goethite varies over 2 orders of magnitude as a function of the mesoscopic heterogeneity of the phases involved (D. Sverjensky, personal communication). It is very difficult, if not impossible, to isolate and uncouple these contributions experimentally; understanding these processes almost always requires the use of model systems, where the contributions can be theoretically decoupled. At present, the overall mechanisms and magnitudes of nanoscale influences on chemical reactivity are not understood even qualitatively.

We take a decidedly multiscale perspective in this review and de-emphasize some natural links between molecular modeling and nanoscience such as the evaluation of surface energies (Wasserman et al., 1997) and polynuclear ion structure and reactivity (Rustad et al., 2000). These are important connections, but, from the point of view of computation, are covered as completely as presently possible in the recent RiMG volume on molecular modeling theory (Cygan and Kubicki, 2001). The downside of this emphasis is that, at least in mineralogy, the field is wide open. There are no papers focused on multiscale approaches to computational modeling in the mineralogical sciences, and far too few papers are focused on multiscale description of mineralogical systems. This more or less remains true even if we open the scope to all of chemical physics. At least as far as modeling is concerned only a few research groups are taking on these types of problems. On the other hand, the multiscale approach is much better developed in the geophysical literature (Yuen et al., 2000).

This chapter is therefore aimed at giving the Earth scientist or mineralogist a simple introduction to the techniques and concepts necessary for approaching nanoscale phenomena such as are associated, for example, with the largest three scales in Figure 1. We begin with an elementary introduction to scaling concepts and the computational description of complex patterns, for example, using wavelets. We then review multiscale
computational physicochemical modeling techniques for solids and fluids with applications in interfacial reactivity, phase separation, and particle agglomeration. Examples are drawn from the chemical physics literature that should resonate with the geochemist or mineralogist.

MULTISCALE DESCRIPTION OF COMPLEX SURFACES

For the kinds of problems characterizing the middle regions of Figure 1, even just model construction presents a serious difficulty. As we pass through the nanoscale regime, we move from systems having simple, straightforward initial conditions, such as the ideally terminated slab shown in Figure 2a, to those that do not, such as the partially oxidized iron nanoparticle shown in Figure 2b. The easy “virtual sample preparation” tasks needed for Figure 2a become considerably more challenging in Figure 2b. The essential problem is one of timescales: even if the molecular-scale phenomena one might wish to simulate occur, or can be made to occur, on nanosecond MD time scales, the processes creating the surface shown in Figure 2b occur on much longer time scales, far outside those in which there is any hope of simulating the evolution of the surface structure directly. Setting up these problems will require close integration of different microscopies, techniques of imaging science, and simulation.

Indeed, while glancing through atlases of mineral surface micrographs such as are found in Schwertmann and Cornell (1991), Cornell and Schwertmann (1992), or Dixon and Weed (1989), and through more recent work on biogeochemically produced minerals (Frankel and Blakemore, 1991; Orme et al., 2001; Banfield et al., 2000; Zachara et al., 1998; Maurice et al., 2000) and minerals formed from aggregation of nanocrystallites (Penn et al., 2001b), one cannot help being struck by the morphological complexity of so-called “kinetically roughened” mineral surfaces formed in non-equilibrium low-temperature environments. One clearly needs new tools in addition to x-ray crystallography to characterize these systems. Although the terms “unit cell,” “Bravais lattice,” “space group,” and “Miller index” are familiar to any geology student, the terms, “self-affine,” “mother wavelet,” and “dynamic roughness exponent” are not. But such concepts are needed to approach the types of problems associated with Figure 1.

Scaling concepts

All of us have probably seen impressive atomic scale micrographs of nearly perfect silicon or gallium arsenide crystals. These pictures convey the concept of a perfect surface perturbed by a set of relatively well-defined defects. Kinetically roughened natural mineral surfaces in low-temperature environments are far more complex, with “defects” occurring on all scales. What is a kinetically roughened surface? A good pedagogical analogy is the game of Tetris, which many people have played and which has been used as a model for the compaction of dry granular media (Caglioti et al., 1997). One begins with an idealized flat surface on a square lattice. Growth units (possibly of several different shapes) are introduced at a certain rate from above, and the player manipulates the $x$ positions and orientations of these units to obtain a surface that is as uniform as possible. When any value of the height $h(x)$ exceeds a maximum value, the game is over. As a reward for achieving an efficient packing density, if a fully occupied layer forms in the system, the maximum height is increased one unit. The score is based on the number of units deposited before the end of the game. At a very slow rate of growth, optimal fits are found easily and the surface remains relatively smooth as a
function of time. At very fast rates of growth (or for complex distributions of growth units), the game becomes more difficult, the growth surface becomes quite rough, and the game ends quickly. The amount of roughening clearly scales with the rate of introduction of the growth units; hence, the term kinetic roughening.

Two fundamental scaling parameters characterize the morphology of rough surfaces as a function of time \( t \) and particle size \( L \). First, the width of the interface \( w = h_{\text{max}} - h_{\text{min}} \) is generally found, empirically, to scale with time according to a power law:

\[
w(L, t) \propto t^\beta
\]

\( \beta \) is known as the growth exponent. As time goes on, the surface gets rougher in the sense that its width increases. However, it is also generally observed that this roughness increases only up to a certain saturation point, after which the surface roughness is constant at \( w_s \).

Second, it is found that the larger the particle, the greater the roughness at the saturation point. This is also found (again empirically) to follow a power law:

\[
w_s(L) \propto L^\alpha
\]

\( \alpha \) is known as the roughness exponent.

What is the fundamental machinery behind the power-law scaling? As a very simple illustration, imagine taking the trace of a surface of a small particle and magnifying it uniformly in all directions. Clearly in this case, \( w_s \) scales as the first power of \( L \) and \( \alpha = 1 \). The uniform scaling indicates a self-similar surface. The scaling need not be uniform. For example, consider Figure 3, consisting of a nested arrangement of lines recursively copied onto itself over four decades in scale. Moving upward, at each iteration, the length scale expands by a factor of 4 and the height by a factor of 2. Hence, the scaling still follows a power law, but now the roughness exponent is one-half. In this case, the surface is said to be self-affine, a less restrictive sort of self-similarity in which the scaling relation is not uniform.

Self-similarity is a key concept in understanding scaling (Falconer, 1990; Barenblatt, 1996; Turcotte, 1997; Meakin, 1998). The origin of self-similarity or self-affinity can be roughly understood in terms of fundamental growth units assembling themselves into larger units. These larger units then constitute a new set of fundamental particles that assemble themselves into still larger units, and so on. The situation is not always so transparent, but somewhere backstage this type of process goes on to generate the power-law scaling.

What about the existence of \( w_s \)? What determines the saturation? Surprisingly, this question is not easily answered. The origin lies in finite size effects and correlations in surface topography due to frustration of atomic surface rearrangements. When the correlation length, the length scale over which height information is communicated, approaches the system size, the width saturates. Clearly, as \( L \) approaches infinity, so does that saturation width. As \( L \) shrinks, the width becomes vanishingly small. This is perhaps evident in the regular surfaces of very small nanoparticles (Penn and Banfield, 1998). These are only the most elementary concepts in an immense literature with several excellent textbooks, including Barabasi and Stanley (1995) and Meakin (1998).

In mineralogy, very little work quantifying these scaling laws has been done, and no studies to date have considered the dynamic scaling problem as applied to surfaces. In
part, this is due to the difficulty of obtaining contiguous data over sufficiently long length scales and sufficiently high resolution to determine accurate scaling exponents. Pioneering examples are work done on goethite by Weidler et al. (1998) and Liu and Huang (1999). Titanium dioxide has received attention in the photocatalysis community (Xagas et al., 1999; Lee, 2001). Cardone et al. (1999) have studied MnO$_2$ and chalcopyrite from the standpoint of fractal geometry. Much more experimental work on multiscale aspects of mineral surfaces and aggregates will doubtless be forthcoming.

Wavelets and multiscale description of surfaces and interfaces

One of the most crucial issues facing scientists today is the flood of data generated by more accurate laboratory measurements and higher-resolution numerical simulations. If we are to perceive some succinct patterns buried in the large arrays of numbers or pixels, fast and efficient techniques are required. We cannot afford to be looking at the data at full resolution all the time because of the time-consuming process in visualizing gigabytes to terabytes of data. Feature extraction is a technique whereby we can distill the most essential aspects of the data, such as the outline of a skeleton in a biological organism or the peaks and valleys of a complicated terrain. Wavelets (e.g., Holschneider, 1995; Bowman and Newell, 1998) mostly developed over the past 17 years present an ideal and relatively easy-to-master tool for extracting certain outstanding scales of interest. They are numerical filters able to zoom in and out in both a given location in physical space and magnification and scale in wavelet space. On the other hand, the traditional method of Fourier analysis yields only a global type of information and loses local knowledge, such as the place or time of the particular phenomenon. Wavelets are linear mathematical transformations (e.g., Resnikoff and Welss, 1998) that can analyze both temporal signals and spatial images at different scales. The wavelet transform is sometimes called a mathematical microscope. Large wavelets give an approximate image of the signal, while smaller and smaller wavelets zoom in on small details.

Until recently, most of the applications of wavelets in geoscience have been focused on geophysical applications—for example, the use of one-dimensional wavelets to analyze time-series of the Chandler wobble or one-dimensional spatial tracks such as topography and gravity anomalies. Recently, fast multidimensional wavelet transforms (Bergeron et al., 1999, 2000a, 2000b; Yuen et al., 2000), based on second-derivatives of the Gaussian function, have been developed, allowing us to construct rapidly two- and three-dimensional wavelet-transforms of geophysically relevant fields, such as geoid anomalies, temperature-fields in high-Rayleigh-number convection, and mixing of passive heterogeneities. These same techniques will be useful also for characterization of mineralogical/geochemical systems. They have already been put to use in materials science investigations involving high-resolution transmission electron microscopy (HRTEM) (Jose-Yacaman et al., 1995) and in atomic force microscopy (AFM) (Duparre et al., 1999; Moktadir and Sato, 2000).

We can define the wavelet transform $W(a, b)$ as the transformation of a signal $f$ in Cartesian space by the three-dimensional integral

$$W(a, b) = \frac{1}{a^{3/2}} \int_0^{L_x} \int_0^{L_y} \int_0^{L_z} f(x) \psi \left( \frac{x - b}{a} \right) a^3 x$$

(3)
where $L_x$, $L_y$, and $L_z$ are the lengths of the periodic box in Cartesian space, $a$ is the scale or the magnification and $b$ is the position vector. The mother wavelet, also known as the convolution kernel or filter (Yuen et al., 2001), is given by $\psi(a,b)$. We have used the higher-order derivatives of the Gaussian function for computational purposes because of its analytical advantage in the transformed domain during the convolution process (Yuen et al., 2001). Instead of having a single parameter, the wave number $k$ in Fourier analysis, there are now two parameters in isotropic wavelets, namely, $a$ and $b$. This will increase the dimensionality of wavelet transform by one. Thus, a one-dimensional wavelet transform needs a two-dimensional plane $(a, b)$ for describing its distribution, while a two-dimensional wavelet transform would need a three-dimensional volume $(a, b_x, b_y)$ for portraying its multiscale distribution on a plane. For one-dimensional data, these plots are commonly shown for time series (Gibert et al., 1998; Vecsey and Matyska, 2000) or in spatial domain over the Laurentide ice sheet (Simons and Hager, 1997).

Wavelet analysis has great potential in image processing applications of interest in mineralogy (see Moktadir and Sato (2000) for an illustrative example for silicon). As an illustration, in Figure 4 we show a version of Equation (3) over a one-dimensional trace across a two-dimensional AFM image of a hematite surface where there are some traces of bacterially mediated reduction reactions. One-dimensional wavelets with the second-derivative of the Gaussian function, also known as Mexican-hat wavelets because of their shape, are used over this path. The inset shows the contours of the function $W(a,b)$ plotted over the $(a, b)$ plane, with the ordinate being the scale and the abscissa the position $b$ along the path. Long-length scale features are shown for $a$ near zero, with smaller-scale features being displayed with increasing value of the scale along the descending direction of the ordinate. One can discern clearly the two sharp peaks of high strength in $W(a,b)$ and how they correlate directly with the two precipitous drops in the path topography. Also note the loss of the long-length scale features in the biologically dissolved region.

One can improve on the resolvability of the fine structures in Figure 4 by using a mapping involving the display of the two proxy quantities $E_{max}(x)$ and $k_{max}(x)$ as a function of the horizontal axis $x$, where $E_{max}$ is the maximum of the L2-norm of the $W(a, b)$ over all scales $a$, and $k_{max}$ is the local wave number associated with the scale $a_{max}$, where $E_{max}$ takes place. This is a form of data-compression, in which one focuses only on the maximum strength of the wavelet signal. It has been used successfully to look at three-dimensional data sets such as three-dimensional tomographical models of the mantle (Bergeron et al., 1999) and gravity signals on the Earth's surface (Yuen et al., 2001). These same techniques, which have proved to be successful in global geophysics, can be brought to bear also on nanoscale phenomena in mineral physics and be equally promising, because we are dealing with Cartesian geometry. Wavelets have been applied in similar contexts in the analysis of shell growth in biomineralization (Toubin et al., 1999).

In the future, high-performance computing will play an increasingly important role in image analysis. One can imagine eventually taking Figure 2b and “photocopying” an atomically resolved representation suitable for use, for example, as initial conditions in a molecular simulation. Such applications would require integration of multiple imaging methods (AFM, scanning tunneling microscopy [STM], other scanning probe microscopies, nuclear magnetic resonance (NMR) HRTEM) with multiscale extrapolations to selective atomic-scale resolution.

MULTISCALE SIMULATION METHODS FOR SOLIDS

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Molecular simulation methods at various scales are shown in Figure 5. Many of these methods are undoubtedly familiar to the reader. At the smallest scale are the electronic structure methods used to describe the formation of chemical bonds. These include Molecular Orbital (MO), density functional (DFT), and the so-called “tight binding” (TB) or semi-empirical methods. In molecular dynamics (MD) methods, the electronic degrees of freedom are parameterized out of the system, and we are left with atoms that interact with each other with pair-wise or higher-order interaction potentials. At the largest scales, the atoms are parameterized out of the system, and we are left with a mesh of finite elements that respond elastically (or viscoelastically) to driving forces at the boundaries of the system. On the left-hand side of Figure 5 lie the so-called kinetic Monte Carlo (KMC) methods, in which the atoms remain but the atomic degrees of freedom are projected out of the system, and in which the atoms are assembled not of their own accord but according to assumed probabilities for growth, dissolution, or reorganization events.

When phenomena at different scales are highly coupled, multiscale modeling methods, which simultaneously treat processes at disparate scales, are required. Many such examples are concerned with dynamically evolving chemical bond formation/dissociation in the presence of a continuum field. Crack propagation is a classic example of this type of inherently multiscale problem, involving close coupling between bond-breaking processes within the crack, elastically nonlinear response near the breaking bonds, and elastic or viscoelastic response at still longer scales. As the crack propagates, regions once allowing a simple continuum description may require atomistic treatment at later times, depending on where the crack decides to propagate. Here, as in other problems, much is gained by allowing for dynamic or adaptive multiresolution in which the relevant scale changes with time in a given region.

Another more mineralogically relevant example is crystal growth by assembly of polynuclear clusters or nanoparticles in aqueous solution (Penn and Banfield, 1998). As the particles or clusters approach each other, hydrolysis of outer hydroxide functional groups yields water molecules that are eliminated progressively from the interfacial region. At some later time, the particles are attached and no longer require an atomistic description at the shared interface. The oxidation of a metallic nanoparticle such as shown in Figure 2b would be another example of an inherently multiscale problem.

**Large-scale molecular dynamics methods**

The simplest approach to multiscale modeling is simply to enlarge the size of an MD calculation so that it spans many scales. Beginning in approximately 1990, million-atom MD simulations were being carried out on parallel computers (e.g., Swope and Anderson, 1990). Parallelization is relatively simple for particles subject to short-range interactions such as exhibited by Lennard-Jones atoms (Smith, 1991; Plimpton, 1995). One simply sorts the atoms into different regions and carries out the force evaluations for each region in parallel with the other regions. Long-range coulombic interactions essentially require that interactions be computed for all \( i, j \) pairs in the system, with no cutoffs allowed. Some researchers, however, do cut these interactions at some finite range. Alternatively, one can obtain machine precision for the coulomb sum using the fast multipole method (FMM) developed by Greengard and Rokhlin (1987). In multipole methods, the long-range interactions are expanded in multipoles, eliminating the need to evaluate every \( i, j \) interaction. The multipole methods were used originally in the context of gravitational
simulations (Barnes and Hut, 1986). What distinguishes the Greengard-Rokhlin FMM is the introduction of a local expansion in addition to the far-field multipole expansion. When only the far-field expansion is used, one obtains $O(N \log N)$ scaling. When both the far-field and local expansions are used, the method scales as $O(N)$. See Kalia et al. (2000) for discussion of the FMM as well as strategies for parallel implementation. While the FMM is the method of choice for systems with $N O(10^6)$, others such as particle-mesh Ewald summation (Straatsma et al., 2000) may be competitive for smaller sample sizes. Another promising approach is to use specialized hardware (GRAPE) designed at the chip-level for rapid computations of pair-wise energy and force evaluations (Higo et al., 1994, Hut and Makino, 1999, also see http://mdm.atlas.riken.go.jp )

An example of some interest in mineralogy is the calculation of the oxidation of a metallic Al nanoparticle carried out by Campbell et al. (1999). In this study, a spherical crystalline metallic Al particle with a radius of 20 nm (252,158 atoms) was placed in an atmosphere of 265,360 O$_2$ atoms confined in a hypothetical container of radius 40 nm (at which reflecting boundary conditions are imposed). The equations of motion for the system were integrated for approximately 500 ps. The system was maintained at a temperature of 400 K. The major findings were that large stress gradients on the order of 1 GPa/nm controlled the diffusion of atoms into the nascent oxide layer. The saturated oxide thickness was in good agreement with experimental measurements of oxide layer thickness measurements in real systems. The oxide layer formed was a mixed octahedral-tetrahedral amorphous phase with a density about 75% of corundum.

As impressive as this calculation is, it still leaves us well short of being able to describe the system illustrated in Figure 2b, where the oxide layer is clearly crystalline. The thickness of the oxide layer may not be strongly influenced by the crystallinity, but certainly the chemical reactivity of the oxide layer will be influenced by nanometer-scale heterogeneities. The question of the actual structure of the oxide layer is entirely outside the range of direct MD simulation, even with the best computers and state-of-the-art computational techniques. Thus, if we want to use simulation to help answer geochemical questions—for example, why do iron nanoparticles of different sizes give rise to different reaction products in the reduction of nitrate (Choe et al., 2000) and CCl$_4$ (Lien and Zhang, 1999)—a different approach is required.

**Coupling methods**

In some cases, it may be desirable to treat different parts of the system under consideration using different methods and use a truly multiresolution technique. This approach is illustrated in Figure 6. The example used here is the attachment of two oxide particles in aqueous solution. During this process, core atoms can probably be treated differently from reactive surface atoms. One might, in fact, abandon an atomistic representation of the core in favor of a continuum model. Solvent far removed from the active regions also could be treated by continuum methods. However, the interfacial water, especially that generated from dewatering reactions $2SOH \rightarrow SOS + H_2O$ (where S represents a surface cation) occurring during grain boundary healing, will need to be treated atomistically.

The general approach of simultaneously treating multiple-length scales has been pioneered by several research groups (Tadmor et al., 1993; Bulatov et al., 1998; Broughton et al., 1999; Tadmor et al., 2000; Rafii-Tabar, 2000; Rudd and Broughton, 2000). The general idea, of course, is to embed one type of calculation into another type of calculation. The concept is familiar in computational chemistry (Cramer and Truhlar,
1991; Fisher et al., 1991; Gao and Xia, 1992; Tomasi and Persico, 1994). Broughton et al. (1999) provide a very clear and detailed discussion of the various issues involved in coupling the electronic structure, molecular dynamics, and finite element regions; we refer the reader to that paper for further discussion of these issues.

Here it suffices to say that the coupling interface between the finite element mesh and the atomic coordinates in the molecular dynamics is accomplished through resolving the near part of the finite element mesh on the atomic coordinates. On either side of the interface, the atoms and the finite element mesh overlap. Finite element cells that intersect the interface and atoms that interact across the interface each contribute to the Hamiltonian at half strength. See Rudd and Broughton (1998) for further discussion of the relationship between molecular dynamics and finite element methods.

In the studies discussed in Broughton et al. (1999), semi-empirical tight binding methods were used to represent the electronic structure. Tight binding methods are gaining popularity in large-scale simulations requiring a representation of the electronic structure (Schelling and Halley, 1998; Frauenheim et al., 2000). In tight binding methods, orbitals \( \phi_{ia} \) are imagined at each atomic center \( i \); for example, one might consider an \( s \) and \( p_x, p_y, p_z \) orbitals on an oxygen atom. The Hamiltonian matrix elements \( \langle \phi_{ia} | H | \phi_{jb} \rangle \) are then parameterized based on empirical data or density functional theory (see Slater and Koster, 1954; Papaconstantopolous, 1986). There are several reasons for using tight binding methods for the electronic structural part of the problem. Foremost, they are the most generally applicable and most commonly used electronic structure methods that can be applied to from hundreds to thousands of atoms in a reasonable amount of computational time. Second, the inherent flexibility of the tight binding approach allows creativity in coupling the tight binding region to the MD region.

In Broughton et al. (1999), the boundary between the tight binding region and the MD region was occupied by fictitious atoms (“silogen” atoms) whose tight binding parameters are modified to give the correct Si-Si bond length, binding energies, and forces. This is similar to the familiar technique of terminating a cluster representation of an extended system using hydrogen atoms (Gibbs, 1982) but now with the possibility of modifying the hydrogen atoms to couple with the MD region. These modified atoms are not coupled directly with each other in the tight binding Hamiltonian but they experience forces due to other non-silogen atoms in the tight binding region as well as from the MD region.

**Transition state searching and kinetic Monte Carlo techniques**

The major limitation of the approaches to multiscale modeling discussed thus far is the timescale. In each of these examples, there are atomic vibrations (on the order of \( 10^{-14} \) seconds) that need to be followed. This pins down the total simulation time to \( O(10^{-9}) \) seconds for reasonable calculations. There are many clever multiple time step methods for improving efficiency (e.g., Nakano, 1999) by using a quaternion/normal mode representation for atoms that are simply vibrating or rotating, but this buys only a factor of \( O(10) \).

In some kinds of systems—for example the “mineral part” (or even the near interfacial water) of the mineral-water interface—the time evolution of the system is characterized by uneventful periods of atoms vibrating around some average location. Only infrequently do some of them collectively assemble, pass through a transition state, and make an interesting conformational move. One needs to somehow “fast-forward” through the tedious parts of the simulation, find the interesting scenes, and use those to
advance the system from state to state. The idea is to search explicitly for transition states instead of randomly stumbling around and taking the first one that comes along.

For small numbers of particles, there are “mode following” methods familiar in quantum chemistry, based on either explicit evaluation of the matrix of second derivatives or guesses at this matrix using first derivatives, and using the normal modes to locate transition states. This explicit method scales poorly with the number of atoms and is not feasible in large-scale simulations. Henkelman and Jónsson (1999) have suggested the so-called “dimer method” for saddle point searches. In this method, two system images slightly displaced from one another are used to define the direction of lowest curvature. Having defined this direction, the dimer is translated based on an effective force in which the force component along the direction of lowest curvature is inverted, driving the system toward a saddle point. Sørenson and Voter (2000) have suggested a method (temperature accelerated dynamics) in which multiple transition paths are located through standard high-temperature MD simulations restricted to a single conformational state. The simulation performs periodic quenching to check whether a new state has been obtained; the criterion is changes in atomic positions in the quenched configurations. If a new configuration is detected, the transition state is located using the nudged elastic band method Henkelman et al. (2000) that solves the problem of locating a transition state between any two local minima. Using these methods, processes on the order of hours can be investigated with molecular modeling approaches.

As yet, these methods have not been applied in very large-scale simulations, but Henkelman and Jónsson (1999) have shown that the method is relatively insensitive to increasing the phase-space dimensionality of the system, so long as the system is large enough to allow all collective relaxations to take place.

The limitations of this theory are: (1) the applicability of harmonic transition state theory (which is rarely an issue for the kind of accuracies typically required in geochemical/mineralogical problems) and, (2) the sparsity of transition states: the dimer method, as presently formulated, finds any transition state. If many of these are not of interest, as might be the case for diffusion barriers on the “water” side of the mineral-water interface, the method would be impractical. This points out another advantage to the multiresolution approach: keeping the extra degrees of freedom of atoms in a region where one could get by with a continuum approach would, for example, require a reformulation of the dimer method.

In some cases, it may be possible to guess at the complete registry of configuration possibilities and kinetic processes. For example, atoms may be fixed on a specific lattice, and events such as attachment or dissolution may be assumed to occur with a specified probability on this fixed lattice. The system then evolves via Monte Carlo simulation over the degrees of freedom permitted by the events that are assumed to occur (Voter, 1986). This type of simulation is referred to as the “kinetic Monte Carlo” (KMC) approach. There have been several applications using this method to simulate crystal growth in mineralogical systems (Blum and Lasaga; 1987 Wehrli, 1989; McCoy and LaFemina, 1997). The obvious drawback to this method is that the elementary processes can come only from the imagination of the investigator. Some surface relaxation processes in simple metal systems are highly collective, and the fundamental events required for the KMC scheme can be very hard to guess in advance (Feibelman, 1998). Similarly, collective behavior may be indicated on oxide surfaces in the work of Henderson et al. (1998), in which complete mixing of singly and triply coordinated oxide surface sites was observed to take place in hours to minutes. Because the activation barrier for a single exchange is probably prohibitive, the mechanism by which this mixing takes place is
almost certainly highly collective. Despite its shortcomings, the KMC method is really the only approach for large problems on long time scales. Using the transition state searching method in conjunction with the KMC method, to identify collective conformer rearrangements for a traditional KMC approach, may be practical.

**MULTISCALE COMPUTATIONAL METHODS FOR FLUIDS**

Solvent effects on chemical reactivity are very large. For example, it takes approximately 395 kcal/mol to dissociate a water molecule in the gas phase but approximately 25 kcal/mol to do this in water at 298 K. Solvent obviously exerts a profound influence on the rates of chemical reactions as well. Nanoscale hydrodynamic effects couple strongly with nanoscale surface structure heterogeneities (including nanopores) and give rise to strong intrinsically nanoscale solvent effects. Of course, these effects must be described with multiscale models for fluids, which have evolved along lines somewhat different from those for solids. However, the general trend is similar, in that discrete particle methods are used to simulate fluids in complex, irregular environments. Here, we provide a review of discrete particle methods in simulation of complex fluids. The techniques are summarized in Figure 7.

**Dissipative particle dynamics**

Microscopic techniques such as MD and MC are very useful in studying interactions between “primary particles” that form molecules and microstructures. However, MD becomes demanding for simulating larger systems. Most of the computations yield information on microscopic fluctuations, which are inessential in scales of complex fluids ordering. The extension of discrete-particle methods to larger spatial scales can be realized by changing the notion of the inter-particle interaction potential by treating a large-sized particle as a cluster of computational molecules. This idea of upscaling has been followed in the dissipative particle dynamics (DPD) method.

Dissipative particle dynamics (Hoogerbrugge and Koelman, 1992) is one of the mesoscopic techniques based on the discrete particles paradigm (SPH, smoothed particle hydrodynamics is another [Monaghan, 2000]). This off-lattice algorithm (meaning the particles can be anywhere) was inspired by the idea of coupling the advantages of both the molecular dynamics and lattice-gas methods. Unlike atoms in molecular dynamics, the dissipative particles employed in DPD represent mesoscopic portions of a real fluid. Particles can be viewed as “droplets” of liquid molecules with an internal structure and with some internal degrees of freedom. The forces acting between dissipative particles are central and consist of the superposition of conservative $F_C$, dissipative $F_D$ and Brownian $F_B$ components. As in molecular dynamics, the temporal evolution of the particle ensemble obeys the Newtonian equations of motion.

As shown in Hoogerbrugge and Koelman (1992), Marsh et al. (1997), and Español (1998), the interactions among DPD particles are postulated from simplicity and symmetry principles. The DPD forces are mesoscopic because they only resolve the center-of-mass motion of the droplets and do not give any detailed description of their internal degrees of freedom. As was proved in Español (1998), the one-component DPD system obeys the fluctuation dissipation theorem defining the relationship between the dissipative and Brownian forces. Marsh et al. (1997) have given a solid background for DPD as a statistical mechanics model. It provides explicit formulae for the transport coefficients in terms of particle interactions.
These principles ensure correct hydrodynamic behavior of DPD fluid. The advantage of DPD over other methods lies in the possibility of matching the scale of discrete-particle simulation to the dominant spatio-temporal scales of the entire system. For example, in MD simulation the timescales associated with evolution of heavy colloidal particles are many orders of magnitude larger than the temporal evolution of solvent particles. If the solvent molecules are coarse-grained into DPD droplets, they evolve much more slowly and are able to match the time scales close to those associated with the colloidal particles.

Dissipative particle dynamics can be employed also for simulating hydrodynamic instabilities. Dzwinel and Yuen (1999) present the algorithm applied for simulation of thin film falling down the inclined plane. In other studies, such as Clark et al. (2000), Dzwinel and Yuen (2001), and Boryczko et al. (2000), more challenging problems are attacked; for example, droplet breakup and mixing in complex fluids.

In Dzwinel and Yuen (2000a, 2000b, 2001), it was demonstrated that DPD fits very well for simulating multiresolution structures of complex fluids. Typical examples of complex fluids with large molecular structure include microemulsions, micellar solutions, and colloidal suspensions like blood, ink, milk, fog, paints, and partially crystalline magmatic melts (Larson, 1999).

For complex fluids, the gap in the spatio-temporal scales between the smallest microstructures and the largest structures is much smaller than for simple fluids. Dzwinel and Yuen, (2000b) have shown that by using moderate number of particles, we can simulate in two dimensions multiresolution structures ranging from micellar arrays to the large colloidal agglomerates.

**Agglomeration of particles**

Despite the general emphasis on atom-by-atom growth, crystalline materials can grow also by accumulation of units of material larger than a single atom or small atomic cluster. Growth of single crystals by oriented aggregation of clay platy particles is well known (e.g., fundamental particle theory for formation of interlayered layer silicates), as is ordered crystallization of large organic atomic clusters such as proteins and large inorganic polynuclear clusters such as $\text{Al}_{13}$ (see review by Casey and Furrer, this volume) and porphyrins (Lauceri et al., 2001). More recently, the importance of growth of nanocrystals of oxides and zeolites by crystallographically specific attachment and interface elimination has been reported (Penn and Banfield, 1998; Banfield et al., 2000).

Homogenous nucleation is a fundamental step in the crystallization of many solids. The mechanisms by which nuclei form, as well as the pathways for subsequent growth, are of basic scientific interest. Control over these phenomena is essential for materials design and prediction of how materials properties will evolve over time.

Theoretical treatment of nucleation processes has evolved along two directions. Hettema and McFeaters (1996) refer to these, respectively, as “classic nucleation theory” and “the kinetic approach”. The kinetic approach is based on a set of time-dependent coupled ordinary differential equations (the Smoluchowski equation) and chemical rate constants (kernels) that are assumed to have non-integer scaling properties with cluster size. The nucleating systems are described in terms of the distribution of cluster sizes as a function of time.

The Smoluchowski equation is given by
where, in the first term in Equation (4), \(i\) and \(j\) represent discrete particle sizes that combine to form a particle of size \(k\). The second term represents the loss of particles of size \(k\) due to aggregation with other particles of size \(i\). \(\beta(i,j)\) is the kernel that is the rate of collision between particles \(i\) and \(j\).

Most numerical techniques employed for aggregation simulation are based on the equilibrium growth assumption and on the Smoluchowski theory. As shown in Meakin (1988, 1998), analytical solutions for the Smoluchowski equation have been obtained for a variety of different reaction kernels; these kernels represent the rate of aggregation of clusters of sizes \(x\) and \(y\). In most cases, these reaction kernels are based on heuristics or semi-empirical rules.

For complex kernels and for collecting information about aggregation kinetics, many simulation techniques were devised (Meakin, 1998). They are based mainly on diffusion-limited aggregation (DLA) and ballistic off-lattice and on-lattice methods. These methods still are far from physical realism. They can be useful for investigating static fractal structures of large agglomerate in the absence of solvent. Moreover, a low initial concentration of colloidal particles has to be assumed. The rheological properties of solvent and the mechanisms of aggregation change with increasing concentration of particles. The reaction kernels poorly reflect actual cluster-cluster and cluster-solvent interactions, which vary with time. Especially, the kernels must be different for a perfectly mixed system and for a system with well-established clusters.

In Dzwinel and Yuen (2000b), we presented a numerical model in which both the colloidal particles and solvent are represented by interacting particles. The time scales associated with evolution of heavy colloidal particles are many orders of magnitude larger than the temporal evolution of solvent molecules. Therefore, we employ DPD for simulating solvent to bridge the two disparate scales. The DPD particles are larger and evolve much slower than molecules, making it possible to match the time scales close to those associated with the colloidal particles. The difference between colloidal and DPD particles consists in the different particle-particle interactions employed. To avoid fluidization of the colloidal particle system and facilitate aggregation, the colloid-colloid interactions should be conservative; they should posses a hard-sphere core with a very short-ranged adhesive part. They model the electro-chemical and depletion interactions acting between colloidal particles in the real solid-in-fluid mixtures.

As shown in Figure 8, by introducing conservative Lennard-Jones interactions between the colloidal particles, we can simulate the spontaneous creation of micelles and their clustering in two-dimensional crystal arrays (see Figure 8a) and large-scale fractal agglomerates (Figure 8b). The growth of the fractal agglomerates is reflected by the scaling properties of mean cluster size \(S(t)\)—expressed in number of particles—with time. The sophisticated shapes of cluster can be recognized by using a clustering procedure based on the mutual nearest-neighboring distance concept. This procedure is outlined in Dzwinel and Yuen (2000b).

In Dzwinel and Yuen (2000c), we show that in DPD fluid with high concentration of colloidal particles, the growth of average size of agglomerate can be described by the power law \(S(t) \sim t^\kappa\). For \(\kappa = 0.5\), the intermediate DLA regime was found, which spans a relatively long time. The length of this relaxation time depends on physical properties of solvent as well as concentration of colloidal particles. The character of cluster growth
varies with time, and the value of $\kappa$ shifts for longer times from 0.5 to $\approx 1$. This result agrees well with the theoretical prediction for diffusion-limited cluster-cluster aggregation. It says that for $t \to \infty$, the value of $\kappa$ approaches 1 for a low colloidal particle concentration. As shown in Dzwielin and Yuen (2000c), this process cannot be asymptotic for a larger concentration of colloidal particles.

**Coarse-graining dissipative particle dynamics: fluid particle model**

A serious drawback of DPD is the absence of a drag force between the central particle and the second one orbiting about the first particle. The dissipative force $F_D$ representing the dot product of differential velocities between interacting particles and their relative position vector is then equal to zero. This relative motion may produce a net drag only when many particles are participating at the same time (Español, 1998). This cumulative effect requires more particles to be involved and reduces the computational efficiency of the DPD method.

With the aim of coarse-graining DPD, the fluid particle method (FPM), a non-central force has been introduced that is proportional to the difference between the velocities of the particles (Español, 1998). This force exerts additional drag, which produces rotational motion. This would allow for the simulation of physical effects associated with rotational diffusion and rotation of the colloidal beds resulting from hydrodynamics or their mutual interactions.

The fluid particles possess several attributes as mass $m_i$, inertia, position $r_i$, translational and angular velocities, $v_i$, $\omega_i$, and a force law. The “droplets” interact with each other by forces dependent on the type of particles. We use the two-body, short-ranged force $F$ as it is postulated in Español (1998). This type of interaction is a sum of conservative force $F^C$, two dissipative forces with translational and rotational parts $F^T$ and $F^R$, and a random Brownian force $\tilde{F}$; that is,

$$F_{ij} = F^C_{ij} + F^T_{ij} + F^R_{ij} + \tilde{F}_{ij}$$

$$F^C_{ij} = -F \left( r_{ij} \right) \cdot e_{ij}$$

$$F^T_{ij} = -\gamma \cdot m \mathbf{T}_{ij} \cdot \mathbf{v}_{ij}$$

$$F^R_{ij} = -\gamma \cdot m \mathbf{T}_{ij} \cdot \left( \frac{1}{2} r_{ij} \times \left( \mathbf{v}_{ij} \right) \right)$$

$$\tilde{F}_{ij} dt = (2k_B T \gamma \cdot m)^{1/2} W_{ij} \cdot e_{ij}$$

$$T_{ij} = A(r_{ij}) \mathbf{1} + B(r_{ij}) \mathbf{e}_{ij}$$

where $F,A,B$ are weighting functions and $W_{ij}$ is a stochastic tensor defined in Español (1998).

As shown in Figure 9, the FPM model represents a generalization not only of DPD but also of the MD technique. It can be used as DPD by setting the noncentral forces to zero, or as MD by dropping the dissipative and Brownian components. These three techniques also can be combined into one three-level hybrid model. As shown in Figure 9, the three-level system consists of three different procedures representing each
technique invoked in dependence on the type of particle interactions. We define three types of particles:

1. **“Hard” colloidal particles.** The interactions between colloidal particles can be simulated by a soft-sphere, energy-conserving force with an attractive tail. The force vanishes for particles separated by the distance greater than $2.5\lambda$ ($\lambda$ is a characteristic length, equal to the average distance between particles).

2. **“Soft” dissipative particles.** They represent “clusters” of molecules located in the closest neighborhood of the colloidal particles with an interaction range $\geq 2.5\lambda$. The DPD-DPD and DPD-MD interactions represent only the two-body central forces.

3. **Fluid particles (FP).** the “lumps of fluid” particles in the bulk solvent, with interaction range $\leq 1.5\lambda$. Noncentral forces are included within this framework.

Mesoscopic flows are important to understand because they hold the key to the interaction between the macroscopic flow and the microstructural inhomogeneities. This is especially true in colloidal flows, which involve colloidal mixtures, thermal fluctuations and particle-particle interactions. Dynamic processes occurring in the granulation of colloidal agglomerate in solvents are severely influenced by coupling between the dispersed microstructures and the global flow. On the mesoscale, this coupling is further exacerbated by thermal fluctuations, excluded volume effects, cohesive interactions between colloidal beds, and hydrodynamic interactions between colloidal beds and the solvent.

The dispersion of an aggregated composite generally proceeds through three stages, which usually occur with some degree of overlap:

1. **Imbibition** – consisting of spreading off the liquid solvent into the colloidal cluster and reducing the cohesive forces between the colloidal beds.

2. **Fragmentation** – consisting of
   a. *shatter* – producing a large number of smaller fragments in a single event,
   b. *rupture* – breakage of a cluster into several fragments of comparable size,
   c. *erosion* – gradual shearing off of small fragments of comparable size
   (Ottino et al., 2000)

3. **Aggregation** – the reverse of dispersion. Two traditional mechanisms can be recognized:
   a. *nucleation* –the gluing together of primary particles due to the attractive forces,
   b. *coalescence* – the combination of two larger agglomerates to form a granule.

In the framework of the FPM model, we have simulated the dispersion and agglomeration microstructures, which appear during acceleration of a slab in FPM fluid. Figure 10 displays the moment of the slab disintegration and agglomeration of the slab remnants. The fragmentation occurs due to a shatter mechanism, which is generated by accumulation of a large amount of energy during compression and its fast release in the decompression stage.

In Figure 11, we display the changes of the largest cluster size and thermodynamic pressure with time. Initial compression of the slab and its subsequent decompression causes the largest cluster disintegrating. The following decompression wave is too weak for disrupting cohesion forces, which contributes to the agglomeration of the slab remnants into larger droplets.

Within the FPM, we can extend further the capabilities of the discrete particle method to the mesoscopic regime and show that they are competitive to standard
simulation techniques with continuum equations. These methods establish a foundation for cross-scale computations ranging from nanoscales to microns and can provide a framework for studying the interaction of microstructures and large-scale flow, which may be of value in blood flow and other applications in polymeric flows (Banfield et al., 2000; Schwertman et al, 1999; Hiemstra and VanReimsdijk, 1999).

OUTLOOK

Indeed, the energy and enthusiasm generated by the scientific community's recent focus on nanoscale phenomena presents an opportunity for making a significant leap in the computational geosciences. In the last few years, revolutionary changes have occurred in the types of problems that can be investigated with computational methods because of the growth in computational power. Higher-resolution calculations and laboratory measurements also produce a data deluge, which we must confront if we are to comprehend fully all of the information. Modeling, feature extraction, and visualization techniques all undoubtedly will play important roles in developing conceptual models of what is really important in determining structure-reactivity relationships at the nanoscale. As is often the case in other contexts, we will need to motivate unique interdisciplinary combinations of research techniques not found in a typical academic department, such as molecular modeling, signal processing, scientific visualization, pattern recognition, and artificial intelligence, as well as techniques in the laboratory, like scanning probe and HRTEM microscopies. Such a mode of scientific operation demands a new way of thinking.

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Figure Captions

**Figure 1.** Cross-scaling processes in low-temperature geochemistry and mineralogy.

**Figure 2.** (a) Idealized surface of hematite (001); (b) oxidized nanoparticle of zero-valent (metallic) iron with oxide rind (used by permission of the editor of Applied Physics Letters, from Kwok et al. (2000), Fig. 2., p. 3972). While the initial conditions for (a) are easily produced, those for (b) are extremely difficult to produce, even if techniques are available that can model the system shown in (b).

**Figure 3.** Recursive replacement of the zigzag motif over four decades in length scale (dash-dot-dot, coarse dash, fine dash, solid; *largest scale shown only partially*). This generates a self-affinned surface with a growth exponent equal to one-half. Modified from Barabasi and Stanley (1995).

**Figure 4.** Multiscale aspects of oxide surfaces in aqueous environments. (b) represents a single trace across a hematite (001) surface undergoing biotically mediated reductive dissolution (a). Relatively clean steps 2.6 nm in size on the left of the figure give way to a complex surface morphology on the right side of the image where biotic dissolution was pervasive. The wavelet transform, to $\frac{1}{2}^7$ levels, is shown in (c). (b) provided by Kevin Rosso, Pacific Northwest National Laboratory.

**Figure 5.** Molecular modeling methods at various scales. MO-Molecular Orbital; DFT-Density functional theory; TB-tight binding; QM/MM: hybrid quantum mechanics/molecular mechanics, MD-molecular dynamics.

**Figure 6.** Hypothetical coupling of length scales in the attachment of two hydroxylated oxide nanoparticles in aqueous solution. The crystal cores are represented by continuum finite elements with elastic moduli $\lambda_{ij}$ and dielectric tensor $\varepsilon_{ij}$. The far-field continuum solvent has viscosity $\eta$, dielectric constant $\varepsilon$, and exerts random boundary forces $F_{\text{stoch}}$ on the fluid inside the large sphere modeled using particle methods. SPC is a simple point charge model for water. Dissipative particle dynamics or Lattice Boltzman methods also may be used here. Inside the small spheres are reactive water molecules modeled using tight-binding (TB) approaches. TB is also used to treat reactive surface functional groups.

**Figure 7.** Discrete particle methods for simulation of fluids. LB (Lattice Boltzmann), MD (molecular dynamics), DPD (dissipative particle dynamics), FPM (fluid particle model).

**Figure 8.** Snapshots from spontaneous agglomeration simulated by using an MD-DPD algorithm. (a) crystal arrays compared to (c) chain of titania nanocrystals in pH 3 solution. (b) colloidal aggregates [(c) used with permission of the publisher of Geochimica et Cosmochimica Acta, from Penn and Banfield (1999), Fig. 6., p. 1552.]

**Figure 9.** Three-level fluid particle model for coarse-graining DPD simulations.
Figure 10. Dispersion of colloidal slab made of “hard” MD particles in FPM fluid. (a) dispersion microstructures (DataExplorer surface); (b) view from below (particles are displayed); (c) agglomeration microstructures.

Figure 11. Dispersion of the colloidal slab in the FPM fluid. The plot presents the changes of the largest cluster size and thermodynamic pressure for the particle system with time. Simulation results come from FPM-MD two-level model.
Figure 1
Figure 2
Figure 4
Electronic Structure

(QM/MM)

Classical MD

Transition State Methods

Quasi Continuum

Coarse-graining

Kinetic Monte Carlo
Freedom from atomistic time scales

Finite Elements
viscoelastic response

Figure 5
Continuum crystal $\lambda_{ij}, \varepsilon_{ij}$

TB H$_2$O; SOH SOH$_2$

SPC water/DPD Fluid

Continuum Solvent $\eta, \varepsilon$

Boundary Force $F_{\text{stock}}$

Figure 6
Match MD forces to input data
Match DPD forces to input data
Match FPM forces to input data

Generate initial conditions

Compute forces
$$\mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij}$$

IF $$\mathbf{F}_{ij}$$

MD forces
$$\mathbf{F}_{ij}^c = -V'(r_{ij}) \mathbf{e}_{ij}$$
$$V(r_{ij})$$ – Lennard-Jones

DPD forces
$$\mathbf{F}_{ij} = \mathbf{F}_{ij}^c + \mathbf{F}_{ij}^T + \mathbf{F}_{ij}^R$$
$$A(r) = 0$$
$$\mathbf{F}^T$$ - central

FPM forces
$$\mathbf{F}_{ij} = \mathbf{F}_{ij}^c + \mathbf{F}_{ij}^T + \mathbf{F}_{ij}^R$$
$$\mathbf{F}^T$$ and $$\mathbf{F}^R$$ – non-central

Move particles

MD particle
$$\ddot{\mathbf{r}}_i = \mathbf{v}_i$$
$$\dot{\mathbf{v}}_i = \frac{1}{m} \sum_{j \neq i} \mathbf{F}_{ij}$$
leap-frog scheme

DPD particle
$$\ddot{\mathbf{r}}_i = \mathbf{v}_i$$
$$\dot{\mathbf{v}}_i = \frac{1}{m} \sum_{j \neq i} \mathbf{F}_{ij}$$
leap-frog + Adams-Bashford

FPM particle
$$\dot{\mathbf{r}}_i = \mathbf{v}_i$$
$$\dot{\mathbf{v}}_i = \frac{1}{m} \sum_{j \neq i} \mathbf{F}_{ij}$$
same as DPD
higher order scheme

Figure 9
Figure 11