

Means many things to many people and rapidly developing field. Goal is to give idea of issues and approaches and some lessons learned

Collaborators: C. Denniston, S. Hyun, X. Nie, B. Luan, L. Pei, J. Rottler, S. Chen, J. F. Molinari, J. A. Harrison, N. Bernstein Sponsor: National Science Foundation DMR and CMS



Some References

Overviews of Multiscale modeling:

- F. Müller-Plathe, "Scale-Hopping in Computer Simulations of Polymers," Soft Mat. 1, 1-31 (2003) · G. Lu and E. Kaxiras, Handbook of Computational Nanotechnology, Ed. M. Rieth & W
- Schommerz, Chapter 22. Curtia & Willer "A tomistic/continuum coupling in computational materials science", Modeling Simul. Mater. Sci. Eng. 11, R33-R68 (2003).

General books on computer simulations:

- · Allen and Tildesley, "Computer Simulation of Liquids," Oxford (1987)
- · D. Frenkel and B. Smit, "Understanding Molecular Simulation: From Algorithms to Applications," 2nd Edition, Academic (2002).

References on potentials:

- Beyond Pair Potentials, A. E. Carlsson in Solid State Physics, Edited by H. Ehrenreich and D. Turnbull. Academic Press, San Diego, Vol. 43, p. 1 (1990). Review of effective potential construction.
- Modern Electron n Theory by M. W. Finnis in Electron Theory in Alloy Design, Edited by D. G. Pettifor and A. H. Cottrell, Institute of Materials, London, 1992. Article on first-principles calculations.
- C. M. Goringe and D. R. Bowler and E. Hernandez, "Tight-binding modelling of materials",
- Reports on Progress in Physics 60, 1447-1512 (1997). N. Bernstein, "Linear scaling nonorthogonal tight-binding molecular dynamics for nonperiodic systems", Europhysics Letters 55, 52-58 (2001)

Some More References

- Quasicontinuum references (more at www.gcmethod.com):
- Miller and Tadmor, J. Computer-Aided Materials Design, 9, 203-239 (2002). Curtin and Miller, Mod. and Sim. in Mat. Science and Engineering 11, R33-R68 (2003).
- Renormalization based approaches Curtarolo and Ceder, "Dynamics of an inhomogeneously coarse-grained multiscale system, Phys.
- Rev. Lett. 88, 255504 (2002).
- Wu, Diestler, Feng and Zeng, "Coarse-graining description of solid systems at nonzero temperature," J. Chem. Phys. 119, 8013-8023 (2003). Accelerated Molecular Dynamics
- Check out www.tl2.lanl.gov/home/afv/ for presentations and references on accelerated dynamics. "Extending the Time Scale in Atomistic Simulation of Materials," A.F. Voter, F. Montalenti and T.C. Germann, Annu. Rev. Mater. Res., **32**, 321 (2002). Other methods
- I. G. Kevrekidis, C. W. Gear and G. Hummer, "Equation-Free: The Computer-Aided Analysis of Complex Multiscale Systems, A.I.Ch.E Journal 50 {7} 1346 (2004)
- "Concurrent coupling of length scales: Methodology and application," J. Q. Broughton, F. F. Abraham, N. Bernstein and E. Kaxiras, Phys. Rev. B 60, 2391-2403 (1999).
- Ren and E, "Heterogeneous multiscale method for the modeling of complex fluids and micro-fluidics," J. Comp. Phys. 204, 1-26 (2005). //www.math.princeton.edu multiscale/review.pdf
- Wagner and Liu, "Coupling of atomistic and continuum simulations using a bridging scale decomposition, J. Computational Physics 190, 249-274 (2003).
- Nie, Robbins and Chen, Phys. Rev. Lett. 96, 134501 (2006)

Behavior controlled by processes on wide range of lengths and times 0.1to 1 nm - chemical bond, size of ions, polymer diameter, ... 1nm to 1µm - size of colloid, polymer, actin, microtubule, ... size of defect structures: fibrils, dislocations, surface roughness 1µm to 1mm - microstructure - collections of defects, domains, scale of cells, heterogeneity in composition, .

large scales - hydrodynamic degrees of freedom, global geometry, ...

Why Multiscale?

Polymer fracture: nm polymer \rightarrow 10nm fibril - $10\mu m \text{ craze} \rightarrow 10mm \text{ crack}$





Why Multiscale?

- Behavior controlled by processes on wide range of lengths and times Want to include relevant physics from all scales
- Usual approach \rightarrow Choose scale of interest and use appropriate method for phenomena at that scale. Model at that scale often chosen phenomenologically or fit to experiment.
- Multiscale approach \rightarrow Couple calculations at different scales Two basic paradigms:
- Sequential or hierarchical Do separate calculations at each scale, pass the results between scales \rightarrow coarse-graining or fine-graining Concurrent – Do simultaneous coupled calculations with different resolutions in different regions

Sequential best when clear separation between processes at different scales, relatively homogeneous large scale systems.

Multiscale methods couple descriptions either sequentially or concurrently

1

Single Scale Methods

- Quantum Monte Carlo Full quantum treatment of electron interactions, and perhaps even quantum treatment of nuclei. Exponential increase in computational effort with number of particles → limited to 10-100 quantum particles.
- Electronic structure calculations Treat quantum mechanical nature of electrons finding ground state for fixed nuclear positions. Algorithms that are linear in # of electrons allow thousands of atoms to be treated for picoseconds. Tight-binding treatment → larger systems and times
- Classical Molecular Dynamics and Monte Carlo Coarse-grain to follow only the motion of atoms, including effect of electrons through a classical potential energy that depends only on the positions of nuclei. Depending on complexity of potential energy can treat 10⁷ to 10⁹ atoms for nanosecond and longer times.

Coarse-grained potentials lump atoms together, follow these groups Example: Lump carbon and hydrogens into a single "united atom" or represent a protein by the carbon atoms along its backbone.



Single Scale Methods – coarser scales.

- Particles representing entire polymers, fluid elements, galaxies, ... Solve dynamics with MD or on lattice (Lattice Boltzmann Method) Know that if equations obey conservation laws, particles will follow hydrodynamic equations → solve Navier-Stokes, magnetohydrodynamics
- Slip-link models for polymer dynamics
- Discrete defect dynamics Identify lines or surfaces where there is a defect in the order parameter: dislocation, interface, ... Average out atoms, follow dynamics of defect
- Phase field models Define local free energy that depends on order parameter: concentration, magnetization, nematic director, ...
 Follow dynamics of order parameter assuming overdamped dynamics
- Purely continuum treatment: Elasticity of solids, Navier-Stokes equation for fluid, ...

Coarse Graining in Sequential Coupling

Coarse-graining: Formally want to integrate out fine-scale degrees of freedom (DOF) as in Renormalization Group

- Divide DOF into coarse labeled I, and fine labeled i For equilibrium partition function can formally write:
- $Z=\Sigma_{Li} \exp(-\beta U(\mathbf{u}_i,\mathbf{u}_l)) = \Sigma_{I} \exp(-\beta U'(\mathbf{u}_l))$
 - $\Sigma = \Sigma_{I,i} \exp(-\beta O(u_i, u_I)) = \Sigma_I \exp(-\beta O(u_I))$
 - where $\exp(-\beta U'(u_I)) \equiv \Sigma_i \exp(-\beta U(u_i,u_I))$

However:

- Summation can not be done analytically in most cases of interest, Numerical approximations are difficult
- Dynamic treatments are even harder
- Effective potential U' depends on temperature, density, ...
- while want potential that is transferable to different cases

Common Method of Sequential Coupling

Calculate some quantity with fine-scale description

- eg. pair distribution function, energy, viscosity, elastic constants, pressure-volume curve, Kuhn length, order parameter
- Adjust parameters of coarser description to reproduce fine-scale data
 - \rightarrow Bad parametrization may miss physics
 - \rightarrow Quantities not included in fit may be inaccurate
 - → Very different parameters may fit fine-scale data equally well Best if can calculate parameters directly
 - i.e. viscosity, elastic moduli, boundary conditions

(Historically this approach was often followed using experimental data to calibrate the description)

Fine-graining requires way of reinserting fine-scale structure – not unique in general, so must allow re-equilibration. Can equilibrate at coarse scale, reinsert atoms to find polarizability, ...

Connecting Atomic Simulations to Continuum Theory

Continuum mechanics needs:	
Boundary conditions (BC)	 + Constitutive Relations
velocity or stress	stress vs. strain (rate)
slip, friction, adhesion	viscous, elastic, plastic
Fraditionally:	
Assume no-slip for fluids,	Simple analytic functions
adhesion laws for solids.	viscosity or elastic modulii
\rightarrow Down to what scale do cont	inuum equations apply?
\rightarrow Is there new mesoscopic beh	navior between atomic and bulk?
\rightarrow Do usual assumptions for B	C and constitutive laws work?
Continuum assumes homoge Simple molecules \rightarrow Continu	neity, short-range correlations uum good at a few diameters (3-10
Polymers \rightarrow New behavior of	on entanglement scale
Near phase transition, correla	ation length sets larger scale
Interfacial behavior may be i	nore complicated than assumed





Basics of a Molecular Dynamics Simulation

- → Choose initial positions & velocities of atoms
- → Integrate Newton's equations numerically
- \Rightarrow Calculate forces from positions and potentials
- \Rightarrow Calculate positions & velocities after time step dt
- \Rightarrow Calculate new forces and repeat
- As system evolves
 - → calculate average experimental quantities (stresses, strains, pressure, volume, temperature, energy, heat flow, work, ...)
- \rightarrow follow detailed motion of atoms
- Can work in any ensemble or geometry: Fix energy or temperature, stress or strain, number or chemical potential, ...

Potentials Between Atoms or Molecules				
Ball and spring models \Rightarrow Tomlinson, Frenkel-Kontorova, etc.				
Generic pair potential \Rightarrow Lennard-Jones potential $4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$				
Effect of neighbors on bonds \Rightarrow Embedded atom method for metals				
\Rightarrow Tersoff, Brenner, Harrison potentials for H, C, Si,				
Electronic energies \Rightarrow Find ground state energy of electrons				
using tight-binding or density functional method				
No good method for including excited states (triboluminescence, etc.)				
or of treating atomic dynamics quantum mechanically (T> $\Theta_D/3$)				
More realistic potential \Rightarrow can ask more specific questions,				
⇒but takes longer to calculate force and dt often decreases				
Today's workstation:	total #atoms	time	length	
Quantum electrons	1000	10ps	5nm	
Realistic hydrocarbons	10,000	100ps	10nm	
Embedded atom method	10,000,000	100ps	100nm	
Lennard-Jones	10,000,000	1ns	100nm	





















Slip Boundary Condition • Sharp interface model for slip can only depend on continuum values at wall: $\sigma_{xz}(0)$, $\partial_x \gamma$, $\partial_x c_1$ • Integrating v gives $u_s = \frac{L_s}{\eta_b} \sigma_{xz} + \frac{L_m}{\eta_b} \partial_x \gamma + (\frac{f_1}{c_1} - \frac{f_2}{c_2}) \partial_x c_1$ $L_s \equiv \int dz(\eta_b / \eta - 1)$ $L_m \equiv \int dz(\eta_b / \eta)(\sigma_{xz} - \sigma_{xz}(0)) / \partial_x \gamma$ and f_i reflects drag force from species i

- Usual Navier condition is limiting case $\partial_x {\rightarrow} 0$
- ${\mbox{\cdot}}$ No change in L_{s} by added surface stresses
- Fits detailed simulations











Phase-Field Model of Fluid-Fluid Interface

•If ξ » a \rightarrow coarse-grained F functional of $\rho,$ ϕ •Square-gradient theories

 $F = \int \left\{ \psi(\rho, \phi, T) + \frac{1}{2} K_{\rho} (\nabla \rho)^2 + \frac{1}{2} K_{\phi} (\nabla \phi)^2 + \frac{1}{2} K_{\rho \phi} (\nabla \rho \cdot \nabla \phi) \right\}$ Usually ignore $K_{\rho \phi}$ (odd in ϕ), assume $K_{\rho \rho} > 0$ Often fix ρ , expand ψ as quartic polynomial in ϕ \rightarrow None of these assumptions is good Assume overdamped dynamics: $\partial \phi / \partial t = -c \delta F / \delta \phi$

- Obtain
 ψ and K's from MD measurements of coexistence line, and pressure and linear response near coexistence
- Fit gives surface tension and width that agrees with MD results although not fit to them
 Denniston & Robbins, Physical Review E69, 021505 (2004)







Conclusions for Fluid/Fluid Interfaces

- Square gradient theory quantitatively describes liquidliquid interfaces down to molecular dimensions *if* density and the order parameter are given equal footing.
- Density fluctuations less costly as q increases. Lower surface tension by factor two to four.
- Simpler models may fit static cases but not dynamics
 → miss variations in γ with time, position, etc.















































Conclusions for Crazing

- · Simple model reproduces elastoplastic deformation, craze growth and failure of polymers
- No sharp onset of plastic deformation Shear stress obeys pressure-modified von Mises: $\tau_v = \tau_0 + \alpha p$ Different line for onset of cavitation
- · Entanglements act like chemical crosslinks Limit extension ratio to $\lambda = (l_0/l_p N_e)^{1/2}$ Chains stretched taut over length $N_e/3$
- · Plateau stress S determined by bulk yield behavior $S\lambda = const.$ for fixed potential
- $S\lambda$ scales with bulk yield stress when change potential
- · Distribution of tensions follows universal exponential form, scission controlled by long tail of high tensions
- Simple multiscale model reproduces macroscopic toughness G
- · Crosslinking in bulk can change interfacial toughness

Some Crazy References

- Location of failure: D. Gersappe and M. O. Robbins, "Where do Polymer Adhesives Fail?" Europhys. Lett. 48(2), 150-155 (1999).
- Effect of roughness: J. Rottler and N. O. Robbins, "Molecular simulations of deformation and failure in bonds formed by glassy polymer adhesives," J. Adhesion Science and Technology, **17**, 369-381 (2003). Polymer Yield:
- Fig. 2003. Sequences as a constant societic and rectification of amorphous polymer glasses," Phys. Rev. E64, 051801 (2003). Teled conditions for deformation of amorphous polymer glasses," Phys. Rev. E64, 051801 (2001) and cond-mail/0104494.
 J. Rottler and M. O. Robbins, "Shear yielding of amorphous glassy solids: Effect of temperature and strain rate," Phys. Rev. E in press and cond-mat0302376.
 Craze formation: A. Baljon and M. O. Robbins, "Simulations of Crazing in Polymer Glasses: Effect of Chain Length and Surface Tension," Macromolecules 34, e20041001 (2001).
 E66, 011801 (2003). J. Rottler and M. O. Robbins, "Jamming under tension in polymer crazes," Phys. Rev. E68, 011801 (2003).
- Craze toughness: J. Rottler, S. Barsky, and M. O. Robbins, "Cracks and Crazes: On calculating the macroscopic fracture energy of glassy polymers from molecular simulations," Physical Review Letters **89**, 148304 (2002) and cond-mat/0112006.
- mat/0112000. Interfacial slip: S. Barsky and M. O. Robbins, "Molecular dynamics study of slip at the interface between immiscible polymers," Phys. Rev. E **63**, 021801 (2001). S. Barsky and M. O. Robbins, "Bulk and Interfacial Shear Thinning of Immiscible Polymers," cond-mat/0108405 and Phys. Rev. E **65**, 021808 (2002).

New approach ⇒vary level of detail as needed

 finite-element to treat long-range elastic deformations

 simple potential in nonlinear regions

 detailed electronic calculation where bonds break



Figure 1. The geometrical decomposition of a silicon slab into the five different dynamic regions of the simulation: the continuum finite-element (FE) region, which is not shown in its entire earther, the atmistic molecular-dynamics (MO) angors: the quarkmit hightheriding (FB) region: the FE/MD "handdsking" interface, and the MD/TB "matchinking" interface. The image is the atmixtude alkion alkie, will expanded were of the TB region surrounded by MO atoms. Note that the TB region surrounds the crack sp with broken-bond MD atoms tailing behind the region.