Getting Real!
Thermodynamics and Statistical Mechanics from First Principles for Materials Science and Engineering

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A*b initio* (atomistic) thermodynamics [Ref. 1 and references therein] has evolved into a standard practice in important application areas such as, for example, defects in materials, surface reconstructions, corrosion, and sensing. Important ramifications have furthermore established its use in heterogeneous catalysis and electrocatalysis.

Since the late 1990s the above method is being complemented by what is called the "*ab initio* kinetic Monte Carlo" approach, enabling the correct description of the kinetic processes that govern diverse technologically important processes and/or **the function** of materials.[1] For short time scales *ab initio* molecular dynamics (MD) helps to identify the relevant processes, but its time span is limited to about one nano second. The *ab initio* kinetic Monte Carlo approach then reaches the realistic range (seconds, minutes, and longer). This enabled the first-principles description and understanding of crystal growth and heterogeneous catalysis.[1]

In this talk, I will examine the critical importance of the accuracy of the underlying interatomic interactions, "the base", which is many-body quantum mechanics. The range of validity of state-of-the-art approximations (also force fields) will be assessed, and I will address the concept of a "cascade of increasing accuracy". The latte starts from (sophisticated) force fields and then goes to higher and higher levels of many-electron quantum mechanics and density-functional theory approximations.[2] With respect to the modeling algorithms, I will focus on replica exchange MD, genetic algorithm, and the kinetic Monte Carlo approach. Examples to demonstrate the crucial needs of a reliable description of the interatomic interactions and the significant errors, that result when the interactions (the base of modeling) are not described accurately, come, e.g., from heterogeneous catalysis and biophysics.

[1] K. Reuter, C. Stampfl, and M. Scheffler, "*Ab Initio Thermodynamics and Statistical Mechanics of Surface Properties and Functions*", in: Handbook of Materials Modeling, Part A. Methods, S. Yip (ed.), Springer, Berlin (2005). ISBN-10 1-4020-3287-0, p. 149
[2] S. Bhattacharya, S. Levchenko, L. M. Ghiringhelli, and M. Scheffler, Phys. Rev. Lett. **111**, 135501 (2013); and to be published.

Two-scale analysis of composite plates with in-plane periodic microstructures

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A method of two-scale analysis of composite plates with in-plane periodic microstructures is presented. The overall structure is replaced by an equivalent laminate at macro-scale, each of whose lamina has its own homogenized material properties, and its in-plane, bending and coupling stiffness characteristics can be evaluated by the numerical plate testing (NPT) based on the homogenization theory.

The NPT is realized by finite element analyses with solid elements conducted on the three-dimensional unit cell models with in-plane periodicity constraints only, and the data obtained from the NPT can be used to identify the material properties for all the laminae. Note here that the macro-scale plate is regarded as a laminated composite plate, even if a laminated structure is not assumed for the microstructure.

Our first trial on this development focuses on the linearly elastic materials so that the in-plane, bending and coupling stiffness matrices in the conventional laminate model can be evaluated as macro-scale properties. The second stage of our presentation is extension to NPT with nonlinear materials, in which material properties for each macroscopic lamina are identified with the method of particle swarm optimization or differential evolution with the help of the novel method of NPT conducted on a unit cell discretized with laminated plate elements.

Several numerical examples are presented to demonstrate the processes of NPT and identification of material parameters as well as the homogenization and localization capabilities of the proposed two-scale analysis method.
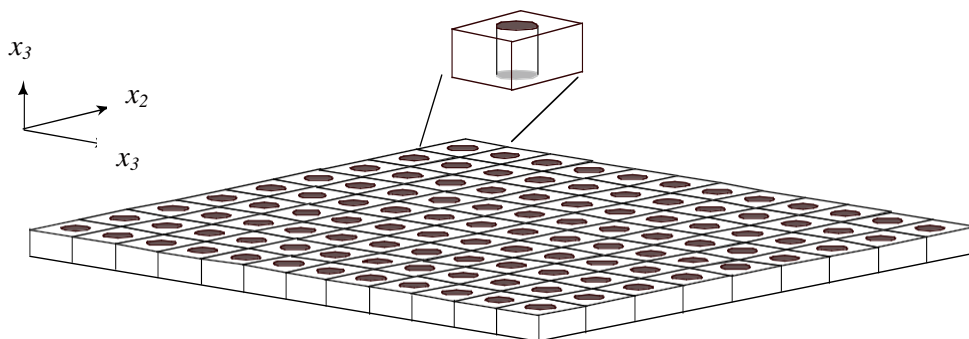
Figure 1: Composite plate with in-plane microstructures

[1] K. Terada, J. Kato, N. Hirayama, T. Inugai and K. Yamamoto, Comput. Mech. **52**, 1199 (2013).

SIESTA-PEXSI: Massively parallel method for efficient and accurate ab initio materials simulation

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We describe how to combine the pole expansion and selected inversion (PEXSI) technique with the SIESTA method, which uses numerical atomic orbitals for Kohn-Sham density functional theory (KSDFT) calculations. The PEXSI technique can efficiently utilize the sparsity pattern of the Hamiltonian matrix and the overlap matrix generated from codes such as SIESTA, and solves KSDFT without using cubic scaling matrix diagonalization procedure. The complexity of PEXSI scales at most quadratically with respect to the system size, and the accuracy is comparable to that obtained from full diagonalization. One distinct feature of PEXSI is that it achieves low order scaling without using the near-sightedness property and can be therefore applied to metals as well as insulators and semiconductors, at room temperature or even lower temperature. The PEXSI method is highly scalable, and the recently developed massively parallel PEXSI technique can make efficient usage of 10,000 - 100,000 processors on high performance machines. We demonstrate the performance the SIESTA-PEXSI method using several examples for large scale electronic structure calculation including long DNA chain and graphene-like structures with more than 20000 atoms.

A coarse-grained Gaussian electronic structure model for molecular dynamics studies of materials

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Computer clock speeds are no longer increasing and increases in computational power are now limited to increases in processor number, unfamiliar territory for computational scientists who have ridden the wave of CMOS-scaling for the past 30 years. In this brave new world, gains in computational accuracy and performance will be driven by methodological development. In this lecture, a non-perturbative treatment of long range forces will be described to allow fast, transferable atomistic simulations is described. There are many physical systems where the non-pairwise additive nature of polarization and dispersion interactions becomes important, in particular, the complex heterogeneous systems of interest in chemistry, biology and biophysics. For example, the dipole moment of water changes from 1.85 Debye in the gas phase to approximately 2.6 Debye in the bulk liquid and attains intermediate values at hydrophobic interfaces due to many-body polarization. Similarly, although the bulk properties of hydrophobic fluids can be modeled using a pair potential, this underestimates the surface tension by 30% due to many-body dispersion interactions. In order to treat both many-body polarization and dispersion interactions in atomic and molecule systems consistently, a coarse grained electronic structure system of quantized Drude oscillators is introduced. Although they obey Gaussian statistics, the system of oscillators generates a surprisingly accurate set of electronic responses as is often the case for models based on Gaussian fluctuations in physics. A simulation method based on quantum path integrals with order O(N) computational complexity is presented to realize the model. Applications to the phase diagram of water and its signature properties, are given.
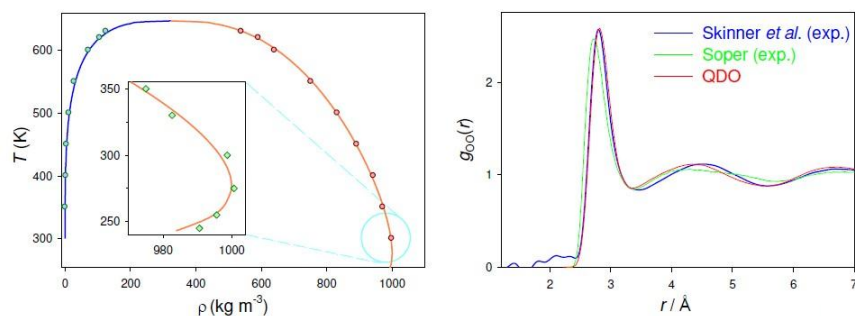
Figure 1: Phase diagram of the Gaussian Coarse-grained water model (left) and its structure at T=300K

A Bayesian Framework for Calibration and Validation of Coarse-Grained Atomistic Models

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The proposed work addresses issues related to the derivation of reduced models of atomistic systems, their statistical calibration, and their relation to atomistic models, particularly those involved with nanostructured materials. In a general sense, an atomistic description of a material contains a listing of the chemical constituents of the material at the atomic scale, as well as a set of mathematical formulas that quantify intra- and intermolecular interactions between the chemical components of the material. These interactions are usually given in the form of a potential energy ansatz containing a set of free parameters that are calibrated in reference to experimental data and highly accurate, but computationally expensive, quantum chemistry simulations. The potential energy forms, once calibrated, serve as the basis for molecular dynamics (MD) simulations that propagate the system forward in time by numerically solving the classical Newton equations derived from the potential energy formulas. Although much faster than quantum chemistry based computations, the described classical methods, referred to as molecular mechanics methods, become prohibitively expensive for systems of millions or billions of atoms. Thus, the theoretical chemistry community is interested in developing reduced models of atomistic systems that are computationally feasible for systems of meso- to macroscopic size (> 10 nm). Popular routes to model reduction include so-called coarse-graining (CG) methods that reduce the degrees of freedom associated with atomistic calculations by replacing particular groups of atoms with single interaction sites (beads). The reduced models derived from the CG procedure, known as coarse-grained models, involve their own sets of potential energy functions, the free parameters of which are commonly calibrated in reference to atomistic simulation data such that the resulting CG models may reproduce aggregate behaviors of the original atomistic models in MD simulations[1]

We pursue a statistical method for CG model calibration based on principles of Bayesian inference[2], the results of which are dependent on the identification of quantities of interest (QOIs) and their related physical observables. The main issues we address here are the derivation of prior CG parameter probabilities from rigorous mathematical principles, the formulation of likelihood functions with respect to relevant physical observables, computational techniques for sampling CG parameter probability distributions, and the analysis of model uncertainty with respect to chosen QOIs. In order to illustrate these issues, we develop a CG model for a liquid heptane system at standard thermodynamic conditions, calibrate CG parameters according to our Bayesian inference framework, and analyze the accuracy and precision of the model's prediction of the vapor/liquid transfer free energy. We conclude that the selection of calibration observables is vital to the well-posedness and predictive ability of a CG model. We also comment on the implications of our method to problems of model validation and selection.

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Assessment of Phase Field Crystal Concepts using Long-Time Molecular Dynamics

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Accelerated molecular dynamics is used to compute the one-particle probability density
in a complex defect consisting of a Lomer dislocation with an equilibrium distribution of
vacancies in the core, and the results are considered within the framework of the Phase
Field Crystal (PFC) model. The computed one-particle density shows numerous spatially-
localized peaks with integrated densities smaller than unity (less than one atom on
average) which correspond to a superposition of just a few specific, well-defined atomic
configurations with well-defined energies and energy barriers between them. There is no
clear path for reconstructing the actual atomic structures from the one-particle density in
the absence of knowledge of the multi-particle correlations. The potential energy
computed using the one-particle density differs from the actual atomistic energy by
nearly 40eV and is distributed among the partially occupied atomic peaks. These results
demonstrate, in one non-trivial case, that the PFC model cannot predict the atomistic
defect structures, energies of those structures, nor kinetic barriers between those
structures. The PFC model thus appears to be limited in its ability to predict atomic defect
properties at the quantitative level needed for application to problems in materials
science.

Modeling the pressure vessel steel microstructure evolution under neutron irradiation using AKMC in Fe multi component alloys - optimization towards long irradiation times

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The ageing and the evolution of mechanical properties of pressure vessel steels under radiation has been correlated with the formation of more or less dilute solute clusters. In the dilute Fe alloys, tomographic atom probe analysis show that these clusters are mainly enriched in Cu, Ni, Mn, Si, P. The evolution of these is governed by the migration of the individual point defects which requires a large number of atomistic kinetic Monte Carlo (AKMC) steps to provide the microstructure state obtained after irradiation. Consequently the simulations are very heavy in terms of computing time. Furthermore, as several substitutional elements (Cu, Ni, Mn, Si, P) and foreign interstitials (C, N) need to be taken into account to describe the alloy, all the possible microstructural objects that can form in the alloys are numerous and complex, their evolution follow very different time scales between the local rearrangement of the clusters and their migration in particular. In this work, some optimization methods and strategies that we have used in our AKMC simulations will be presented and discussed. The microstructure obtained will be compared to experimental results.

Kinetics and micromechanics associated with crack growth in brittle materials

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In this study, kinetics and micromechanics associated with crack growth in brittle materials are considered. It is known that crack growth characteristics contain information on the material strength of fracture mechanisms and that there are sufficient experimental data evidencing that in most cases a crack growth is surrounded by a severely Damage Zone (DZ) which often precedes the crack itself. During its propagation, the DZ is characterized by few degrees of freedom (elementary movements) such as translation, rotation, isotropic expansion and distortion. On the basis of a stress field distribution obtained by the use of a Semi-Empirical Approach (SEA), which relies on the Green's functions, these driving forces corresponding to the mentioned degrees of freedom are formulated within the framework of the plane problem of elastostatics.

A number of theoretical models have been proposed for the description of a stress field and kinetics of a damage zone [1, 2]. The traditional one identifies the DZ as a plastic zone and uses the well developed technique of the plasticity theory for the determination of its size, shape, energy release rates etc… According to recent experimental results, some damage patterns do not yield any model of plasticity and the shape of the DZ can be difficult to model. Then, a plasticity criteria is not adequate for damage characterization. However, elastoplastic solution is currently employed due to the lack of other approaches.

Throughout this study, SEM is proposed for evaluating the stress field and the different energy release rates. This approach is based on the representation of displacement discontinuities by means of the Green's function theory [3, 4]. This latest has been used in a purely theoretical context. Herein, we suggest a more realistic model (arbitrary orientations of discontinuities rather than rectilinear ones) for which the result can be obtained using the experimental data and thus avoiding the difficulties of analytical solutions.

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Quantum-Atomic-Continuum-Coupled Model for the Thermo-mechanical Behavior in Micro-nano Simulation

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In order to study the thermo-mechanical behavior of materials in micro-nano scale, a computational model which couples quantum-atomic-continuum natures together is presented in this paper (i.e. QACC model). Unlike traditional methods, the transition region is not needed since the nonlocal mechanical effects are naturally involved in this model. Some necessary assumptions are made when using first principle density functional calculations. Deformations based on Bravais lattice are explicitly derived.

The responses of 3-demensional 25313 copper atoms nanowires under different external loads are simulated in this paper. Stress and strain fields are calculated and dislocation distributions are predicted in the damage process (shown in Figure 1). Numerical results confirm the validity and transferability of this model.

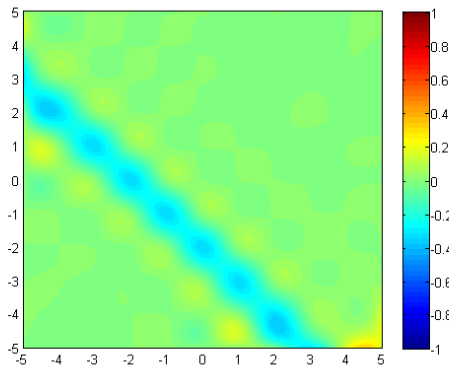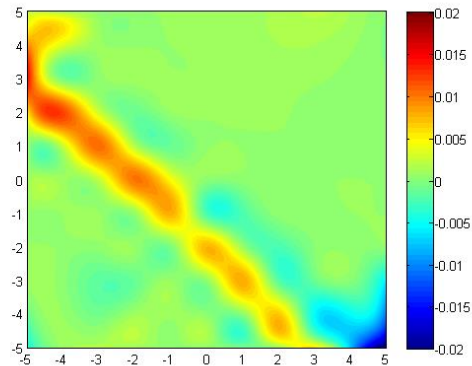
Figure 1 a)   Figure 1 b)

Figure 1 a) xz component of the Cauchy-Green strain tensor and b) xz component of the first Piola-Kirchhoff stress tensor under tension on the middle plane.