

FREE ENERGY CALCULATIONS

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Introduction

In materials science, many important processes such as phase transformations, diffusion, fracture, segregation, the growth of surface layers, surface reconstruction, are sensitive to temperature. There is strong motivation for calculating the free energy changes involved in such processes, since calculations and understanding of the driving forces based on zero Kelvin total energies may be inaccurate or totally inappropriate. Methods for calculating free energy changes include thermodynamic integration, Monte Carlo simulation, quasiharmonic phonons, and others. The aim of this workshop is to bring together people who are interested in such methods and their application, to pool ideas and results. There will be relatively few talks and time will be specifically allocated for discussions between them. It is hoped to strike a balance between methodologies and applications.

Abstracts

Free Energy Evaluation via Quasiharmonic Lattice Dynamics

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In principle, lattice dynamics is an attractive route for the calculation of the thermodynamic properties of crystals with periodic symmetry. Quantum effects are readily taken into account and the method does not rely on long runs for high precision. Unstable vibrational modes provide a sensitive test for interionic potentials and interpretation of the normal modes is straightforward, revealing, for example, the mechanisms of phase transitions or thermal expansion. The kinetic barriers and critical slowing-down effects suffered by Monte Carlo and molecular dynamics techniques are avoided. The bulk of the computational effort is usually expended in the optimisation problem of finding the equilibrium geometry at a given temperature and pressure; given this, calculation of the free energy, heat capacity, thermal expansion etc. is rapid and accurate. We have recently developed a new code, SHELL [1], for three-dimensional ionic crystals and slabs which calculates the full set of free-energy first derivatives analytically and so for the first time a full minimisation of the quasiharmonic free energy with respect to all internal and external variables is possible for large unit cells. Currently short-range interactions are via two and three-body potentials. In this talk the theory [2,3] will be outlined and recent applications discussed, including (i) negative thermal expansion ceramics (ii) surface [3] and defect [4] free energies. Lattice dynamics is also the basis of a recently proposed methodology [5] for obtaining the free energy of disordered solids and solid

solutions, which is quite different from standard approaches. Results for MnO/MgO and CaO/MgO will be presented.

1. SHELL - a code for lattice dynamics and structure optimisation of ionic crystals, M.B. Taylor, G.D. Barrera, N.L. Allan, T.H.K. Barron and W.C. Mackrodt, *Comp. Phys. Comm.* 109, 135 (1998).
2. M.B. Taylor, G.D. Barrera, N.L. Allan and T.H.K. Barron, *Phys. Rev.* B56, 14380-14390 (1997); *Phys. Rev.* B59, 353 (1999).
3. M.B. Taylor, C.E. Sims, G.D. Barrera, N.L. Allan and W.C. Mackrodt, *Phys. Rev.* B59, 6742 (1999).
4. M.B. Taylor, G.D. Barrera, N.L. Allan, T.H.K. Barron, and W.C. Mackrodt, *Faraday Discuss.* 106, 377 (1997).
5. J.A. Purton, J.D. Blundy, M.B. Taylor, G.D. Barrera and N.L. Allan, *Chem. Commun.*, 628 (1998).

Ab Initio Thermodynamics of Matter under Extreme Conditions.

The QUASI Project.

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The talk will describe the QUASI project (Quantum Simulation in Industry), a European funded collaboration developing simulation techniques based on QM/MM (coupled Quantum Mechanical / Molecular Mechanical) schemes and application to industrial problems. The QM/MM method will be reviewed, and the software development aspects of the project described. The functionality of the MD module, currently under development based on elements of the DL_POLY package) will be discussed. Particular emphasis will be given to the use of a Tcl interpreter to control the simulation protocol, statistics collection and constraint terms in free-energy simulations. The target applications for QUASI, spanning biological, zeolitic and surface catalytic systems, will be summarised.

Efficient Calculation of Free Energy from Computer Simulation.

Jeff Rickman

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In the last few years a number of complementary approaches have been devised to obtain free energies from simulation. In this talk I will discuss several such methods including: histogram techniques, cumulant expansions, harmonic approximation schemes and so-called "mechanical" calculations wherein the entropy of a system is determined directly from its region of motion in phase

space. For the purposes of illustration, the results of the application of these methods to various model systems will also be presented. Finally, I will outline some recent progress in the application of stereological techniques to the determination of entropy.

Interfacial and Surface Free Energies in Polymeric Systems.

Dr. Marcus Mueller,

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Surface free energies and interfacial tensions are important for many practical applications (e.g. wetting, coatings, adhesion). We study wetting phenomena and interfacial properties in a binary polymer blend by Monte Carlo simulation of a coarse grained polymer model (bond fluctuation model). Two methods for calculating the interfacial tension shall be discussed: reweighting techniques and the analysis of interfacial fluctuations. Employing an expanded ensemble where the monomer wall interaction is a stochastic variable we are able to accurately measure the surface free energy difference of the two species of the blend at a wall. Both free energies allow a localisation of the wetting transition via the Young equation. For our model of a binary polymer blend we find strongly first order wetting transitions. The consequences for the phase diagram of a mixture confined into a film are discussed.

Free Energy calculations in Molecular Dynamics simulations: Surfaces and Solvation.

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There are a number of methods for calculating changes in Free Energy in Molecular Dynamics simulations. I shall describe three recent rather different calculations which illustrate some of the methods and technical problems involved.

1. Measuring surface free energies of solids with surface melting/disorder [1]. This we did by thermodynamic integration. The technical problem was to find a suitable path to turn off the interaction between slices of a bulk (infinite) crystal to generate slabs with surfaces.
2. Measuring free energy profiles for small molecules passing through the liquid-vapour interface [2]. This was done by measuring average forces in a constrained simulation, and then integrating. The main technical problem were long relaxation times.
3. Measuring ion solvation free energies [3]. We were concerned to find the solvation free energy as a function of charge and size of a spherical solute in water. This was done by a method in which the system with given charge and solute size was embedded in a higher dimensional space

with charge and/or size as additional variables. The variation of free energies in this higher dimensional system with extended dynamics was found from both integrating the forces on the new variables and using the histogram method in a molecular dynamics simulation with extended dynamics.

1. P.Smith and RMLB, Mol. Phys. 96, (1999) 1027-1032.
2. T. Somasundaram, C.Patterson and RMLB Phys. Chem. Chem. Phys. 1, (1999) 143-148.
3. J.Rasaiah and RMLB J. Chem. Phys. 107, (1997) 1981-1991.

Lattice Switch Monte Carlo

Graeme Ackland, University of Edinburgh.

Lattice Switch Monte Carlo is a technique for obtaining free energy differences directly without calculating the absolute free energies. As such, it offers considerable computational advantages over methods which attempt to evaluate the exact free energy. The method requires construction of a bipartite phase space describing the two systems to be compared, and incorporating a Monte Carlo move which switches between regions of space.

A practical application of the method, involving biased sampling techniques, will be illustrated with an example of the free energy difference between the fcc and hcp structures of hard spheres. Further applications of the method will be discussed, including switching between different models for the total energy of a system.

Free Energy Calculations for Defect Processes in the Dilute Limit.

John Harding,

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Point defects in solids affect the vibrational spectrum of the crystal; producing both a general perturbation of the form of the density of states and individual, strongly localised modes ('true' local modes, gap modes and resonances). These effects are an important contribution to the entropy of defect processes and also offer a sensitive test of the model of crystal forces used.

We discuss methods for obtaining free energies of defect processes in ceramics within the quasi-harmonic approximation and the problems of comparison with the (rather limited) experimental data available.