Hybrid Monte Carlo and lattice dynamics simulations: the enthalpy of mixing of binary oxides

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We present two novel methods for the calculation of the enthalpies of mixing of oxides; both the sampling of many different configurations and the effects of ionic relaxation, which have been largely neglected in previous studies, are crucial.

Understanding the thermodynamics of solid solutions of oxides and phase stability is essential in many areas of solid-state chemistry and mineralogy, including the fabrication and design of ceramics, solid-state batteries, heterogeneous catalysis and high temperature superconductivity. However, experimental data are difficult to obtain and are often unavailable. This is particularly acute at high temperatures and/or pressures, where thermodynamic behaviour is important for sustained material performance and for the stability of minerals deep within the Earth's interior. The paucity of experimental data has led to possibly severe approximations such as the extrapolation of low temperature data and the assumption that enthalpies of mixing, ΔH_{mix}, are constant over wide ranges of temperature.

Advances in computational procedures are such that atomistic simulations[1] (*e.g.*, Monte Carlo, molecular dynamics, lattice statics and dynamics) are now capable of providing detailed information about the structure and thermodynamics of ordered inorganic materials and minerals over a wide range of T and P. The vast majority of calculations have studied the properties of perfect crystals, assuming a periodic system in a particular configuration; disorder has largely been investigated theoretically *via* point defect calculations, which refer only to the dilute limit. Such methods are not readily extended to solid solutions or disordered systems containing a finite impurity or defect content. Simulations have been largely restricted to the study of end-member compounds, excluding many industrially important ceramics and naturally occurring minerals.

The key objective of the present work is to show explicitly how (*i*) a modified Monte Carlo technique, that allows an efficient sampling of a large number of different configurations, and (*ii*) direct free energy minimisation *via* lattice dynamics can be used for the study of solid solutions, taking explicit account of relaxation and thermal effects. We do not resort to the use of a parameterised Hamiltonian which averages out local relaxation and cannot readily be extended to include the effects of lattice vibrations and pressure. In this way we remove the major limitations of the existing methods which restrict considerably the contact between experiment and theory, and extend the range of applications that can be tackled to include real rather than model systems.

In this preliminary communication we report results for the enthalpies of mixing of the paradigm system MnO/MgO. We use the ionic model and the set of potential parameters from the work of Lewis and Catlow.[2]

The motivation for our new hybrid Monte Carlo (HMC) approach has been the extensive use made by related techniques in the modelling of polymers and biomolecules.[3–5] During one HMC cycle, one of three options is chosen at random, with equal probability. The first of these is a short NVE molecular dynamics (MD) simulation (15 steps and a timestep of 1.5 fs) in which the last configuration is accepted or rejected by comparing its energy with the energy of the starting configuration and using the standard Metropolis algorithm. If the last configuration is rejected, the original configuration is included in the statistical averaging of thermodynamic properties. In the second, a short MD run follows a random exchange of atoms. Again, the difference in energy between the previous configuration and that immediately after the MD simulation is used in the Metropolis algorithm. This second option allows us to sample efficiently different configurations, while the first mainly takes account of vibrations. At the start of each MD run, velocities are chosen anew at random from a Maxwellian distribution. The third option is a random change of the volume of the box[6] which again is accepted or rejected using the Metropolis algorithm.

In Fig. 1(*a*) we show the values of ΔH_{mix} determined using HMC and a box-size of 216 ions at 1300 K. The enthalpy of mixing at 1300 K is symmetric with a maximum of *ca.* 5.4 kJ mol^{-1} at a concentration of 50% MgO–50% MnO. We have been able to find two sets of experimental data less than thirty years old.[7,8] Agreement with the data of Gripenberg *et al.*[7] is good, but we do not see the asymmetry reported by Raghavan.[8] For comparison we also show values calculated using mean field theory, a common approach to the modelling of solid solutions.[9] In this model, instead of distinct Mg^{2+} and Mn^{2+} ions, a 'hybrid' ion is introduced, for which the non-Coulombic potentials are a linear combination of the potentials for Mn^{2+} and Mg^{2+}, appropriately weighted by the site occupancies. If local relaxation or clustering is important then results from this approach will be poor. Fig. 1(*a*) shows that this is the case even in our relatively simple example, where the Mn^{2+} and Mg^{2+} ions are similar in size.

An alternative approach is to average over a limited set of calculations representing different arrangements of the cations within a supercell. Previous work has often assumed just one (the most regular) arrangement and calculated its energy, with or possibly without relaxation, either using lattice statics/dynamics, or by an *ab initio* method.[10] We have recently developed an efficient method which uses lattice statics and quasiharmonic lattice dynamics (QLD) for the fully dynamic structure optimisation of large unit cells *via* the analytic calculation of the free energy, G, and its derivatives with respect to all strains.[11] Given the free energy, G_k, for the relaxed structure of each possible cation arrangement k the enthalpy is properly averaged over all arrangements in the Gibbs ensemble using

$$<H>=\frac{\sum_k H_k \exp(-\beta G_k)}{\sum_k \exp(-\beta G_k)}$$

Fig. 1(*b*) shows the enthalpies thus calculated of disordered supercells containing 16, 32 and 64 ions of $Mg_xMn_{1-x}O$ (x = 0, 0.25, 0.5, 0.75, 1). For the 16-ion cell, the average was over all possible cation arrangements, whilst for the larger supercells 32

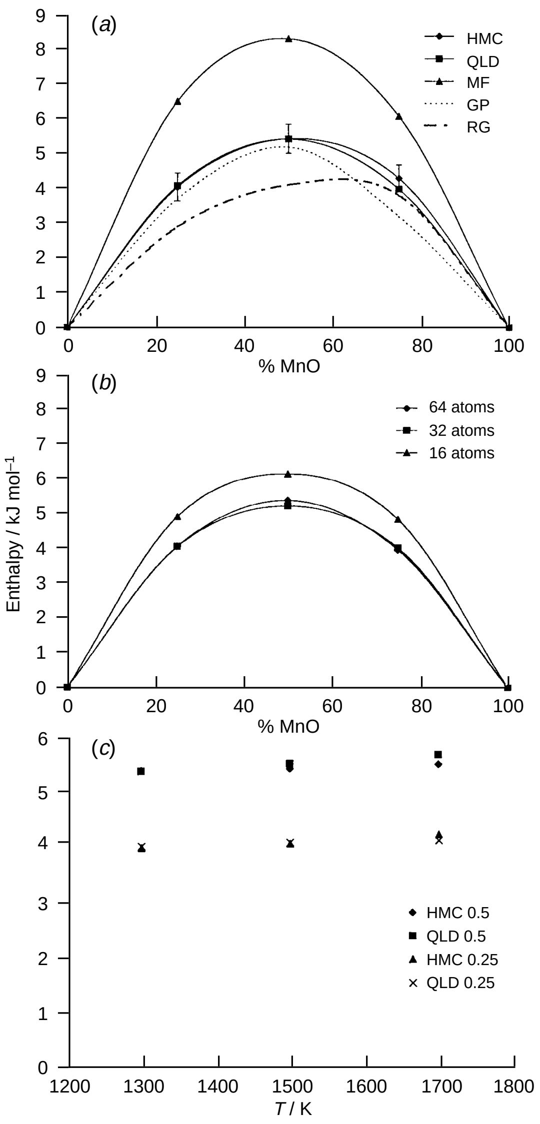

Fig. 1 (*a*) Calculated values of $\Delta H_{\rm mix}$ at 1300 K using hybrid Monte Carlo (HMC), mean field theory (MF), and quasiharmonic lattice dynamics (QLD). Two sets of experimental data (GP from ref. 7, RG from ref. 8) are also shown. (*b*) The variation of $\Delta H_{\rm mix}$, calculated using QLD at 1300 K, with supercell size. (*c*) $\Delta H_{\rm mix}$ *vs.* T for $Mg_xMn_{1-x}O$ (x = 0.25, 0.5), calculated using QLD and HMC.

arrangements were chosen at random for each concentration. The enthalpies for 32- and 64-ion cells are almost identical and are substantially smaller than those from the 16-ion cell. This highlights once again the importance of allowing for relaxation and clustering. The results for the 64-ion cells are also shown in Fig. 1(*b*) where it is clear that there is excellent agreement between the quasiharmonic lattice dynamics and HMC methods. This result suggests the future use of QLD for enthalpies of mixing at temperatures below the Debye temperature where classical Monte Carlo and molecular dynamics fail due to their neglect of quantum effects. Moreover, the Gibbs free energy can be calculated efficiently and accurately from the QLD, without resorting to lengthy thermodynamic integration.

Fig. 1(*c*) shows the calculated temperature dependence of $\Delta H_{\rm mix}$ over the temperature range 1300–1700 K calculated using both HMC and QLD. $\Delta H_{\rm mix}$ does not change significantly with temperature, supporting the common assumption that $\Delta H_{\rm mix}$ is largely temperature independent.

In summary, we have demonstrated that both the proposed HMC and QLD methods provide an accurate description of the enthalpy of mixing of the binary oxides MgO–MnO. We reiterate that it is essential to take explicit account of ionic relaxation without any averaging out of local effects. The methodology we propose is general, easily extended to other ensembles, and applicable to a wide range of materials and minerals.

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Notes and References

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