Beyond the point defect limit: Simulation methods for solid solutions and highly disordered systems

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Abstract

We discuss how two techniques, based on (1) lattice statics/lattice dynamics simulations and (2) Monte Carlo methods may be used to calculate the thermodynamic properties of solid solutions and highly disordered systems. The lattice statics/lattice dynamics calculations involve a full free-energy structural optimization of each of a number of configurations, followed by thermodynamic averaging. The Monte Carlo simulations include the explicit interchange of cations and use the semigrand canonical ensemble for chemical potential differences. Both methods are readily applied to high pressures and elevated temperatures without the need for any new parameterization; at agreement between the two techniques is better at high pressures where anharmonic terms are smaller. Vibrational contributions to thermodynamic quantities of mixing are examined. A range of examples, including binary oxides, garnets and carbonates, are used to illustrate the methods.

Keywords: Solid solutions; Disorder; Simulation; Garnets; Entropy

1. Introduction

Grossly disordered minerals and non-ideal solid solutions, continue to present considerable challenges to the theoretician. The cluster variation method (CVM) [1], for example, widely used for metallic alloys, often performs poorly where species involved are markedly dissimilar, as is usually the case in ceramics and minerals. Using parameterized Hamiltonians (e.g., of Ising type) is increasingly difficult beyond binary alloys. Disorder in ionic materials has often been studied via point defect calculations (the dilute limit). Another route has been via the use of a ‘supercell’ [2], in which a periodic ‘super-lattice’ of defects is introduced, extending throughout the macroscopic crystal; an artificial ordering is thus imposed on the arrangement of defects by the periodic boundary conditions. In this paper we discuss two multi-configuration techniques for solid solutions or disordered systems with a finite impurity or defect content far from the dilute limit. Both of these, unlike the point defect or supercell calculations, sample many different arrangements of ions. Both are readily applied to high pressure and include thermal (vibrational) effects, which have proved problematic for traditional methods [1].

The first of these builds on an efficient method for the fully dynamic structure optimisation of large unit cells...
which uses lattice statics and quasiharmonic lattice dynamics (QLD). The accurate calculation of the free energy via QLD is quick and computationally efficient and does not resort to lengthy thermodynamic integration. The full set of free energy first derivatives is calculated analytically and a full minimisation of the free energy with respect to all structural variables for large unit cells is possible [3]. Here this technique is extended to evaluate the free energies of solid solutions and phase diagrams at any pressure. This is achieved by forming a thermodynamic average of the free energies of a number of configurations. No a priori assumptions are made regarding the configurational entropy contribution; vibrational contributions to thermodynamic quantities at any temperature and pressure are determined straightforwardly. This configurationally averaging differs in some important respects from CVM [4], which defines the energy of the system as an expansion of effective cluster interactions (ECIs). These ECIs are calculated by fitting to the energy of several optimized configurations. A large range of further configurations can then be generated by applying the ECIs within the configuration to calculate their energy. Where the interactions within the system are complex or long-range the number of ECIs that need to be defined in the CVM can make the expansion unfeasible [5]. Generally calculations using CVM do not take the effect of relaxation or vibration into account. The use of quasirandom structures (QRS) allows an estimate of the vibrational contributions to the atomic configuration. The thermodynamic averaging is performed over the results of a set of full free-energy minimisations of configurations and all summations in Eqs. (1) and (2) are restricted to \( K' \), configurations chosen at random. \( K \) in the second term of Eq. (3) is replaced by \( K' \) and

\[
H = \frac{\sum_{k=1}^{K} H_k \exp(-G_k/k_B T)}{\sum_{k=1}^{K} \exp(-G_k/k_B T)}
\]  

(1)

\[
G = -k_B T \ln \left( \sum_{k=1}^{K} \exp(-G_k/k_B T) \right)
\]  

(2)

\( G_k \) is the Gibbs energy for the relaxed structure of each possible cation arrangement. We thus have expressions for any thermodynamic quantity in terms of thermodynamic quantities obtained with particular configurations. The thermodynamic averaging is performed over the results of a set of full free-energy minimisations of different arrangements (configurations) of the cations within a supercell.

For other than the smallest supercells it is impractical to sum over all \( K \) configurations and all summations in Eqs. (1) and (2) are restricted to \( K' \) configurations chosen at random. \( K \) in the second term of Eq. (3) is replaced by \( K' \) and

\[
H = \frac{\sum_{k=1}^{K} H_k \exp(-G_k/k_B T)}{\sum_{k=1}^{K} \exp(-G_k/k_B T)}, \quad \text{and}
\]  

(3)

\[
G = -k_B T \ln \left( K - k_B T \ln \left( \sum_{k=1}^{K'} \exp(-G_k/k_B T)/K' \right) \right)
\]  

(4)

2.2. Monte Carlo simulations

The Monte Carlo exchange simulations (MCX) [12] are carried out within the NPT ensemble. Randomly selected atoms are moved at random in order to take vibrational effects into account. At any step, a random choice is made whether to attempt a random exchange between two atoms, a random displacement of an ion, or a random change in the volume of the simulation box with relative probabilities 1:N:1. To determine whether the change is accepted or rejected, the usual Metropolis algorithm is applied. The maximum changes in the atomic displacements and the lattice parameters are governed by the variables \( r_{\max} \) and \( v_{\max} \), respectively, and these are adjusted automatically during the equilibration part of the simulation to maintain an acceptance/rejection ratio of \( \approx 0.3 \). Calculation of the free energy is less straightforward than with QLD; semigrand canonical ensemble simulations are used to calculate the difference in chemical potential of ions A and B.
The conversion of one species, B into another, A, is considered, and the resulting potential energy change $\Delta U_{B/A}$ determined. This is related to the change in chemical potential $\Delta \mu_{B/A}$ by,

$$\Delta \mu_{B/A} = -k_B T \ln \left( \frac{N_B}{N_A + 1} \exp(-\Delta U_{B/A}/k_B T) \right) \quad (5)$$

Every fifth step of the MCX simulation we evaluate the energy associated with the conversion of a randomly chosen ion type B to ion type A, $\Delta U_{B/A}$ and as the simulation proceeds the average value of the exponential in equation is determined.

3. Results

3.1. MnO–MgO

We start with the solid solution MnO–MgO. Shown in Fig. 1 are values of $\Delta H_{\text{mix}}$ at 1000 K and zero pressure, calculated using QLD and MCX for a 50/50 mixture with a unit cell of 128 atoms and 12,870 randomly chosen configurations. In the QLD all external and internal degrees of freedom are optimized for every configuration; for a detailed study of the convergence properties with cell size and number of arrangements, see Ref. [13]. The MCX simulations used a simulation cell of 512 ions, and $4 \times 10^7$ steps, following initial equilibration of $1 \times 10^7$ steps. The plot shows there is good agreement between QLD and MCX, despite QLD using vastly less configurations than MCX and neglecting higher-order anharmonic terms (though quantum effects are incorporated in QLD). The calculated $\Delta H_{\text{mix}}$ at 1000 K is symmetric with a maximum of 5.4 kJ mol$^{-1}$. No symmetry constraints are applied in any of the calculations. We have examined previously [11] the striking failure of mean-field approach and ‘hybrid’ potentials for $\Delta H_{\text{mix}}$. Entropies of mixing, $\Delta S_{\text{mix}}$ calculated using QLD, include both configurational and vibrational entropies. Fig. 2 plots $\Delta S_{\text{mix}}$ as a function of composition at 1000 K. Note $\Delta S_{\text{mix}}$ is larger than the ideal value for compositions for $x_{\text{Mn}} > 0.25$.

The calculation of the free energy of mixing is a severe test of our model since $\Delta H_{\text{mix}}$ and $-T \Delta S_{\text{mix}}$ are often very close in magnitude. For MnO–MgO in the QLD, 250 configurations with a supercell of 128 atoms are sufficient to ensure adequate convergence in the positions of the two minima in the $\Delta G_{\text{mix}}$ vs. composition curves. It is vital to allow for atomic relaxation, as demonstrated strikingly in Fig. 3 which compares calculated

![Fig. 1. $\Delta H_{\text{mix}}$ (kJ mol$^{-1}$) at 1000 K for MnO–MgO as a function of composition calculated using configurational QLD and using MCX.](image1)

![Fig. 2. $\Delta S_{\text{mix}}$ (J K$^{-1}$ mol$^{-1}$) at 1000 K for MnO–MgO as a function of composition calculated using QLD (filled circles). The points (triangles) labeled LS are values calculated using configurational averaging but with each configuration minimized in the static limit. For comparison the ideal entropy of mixing is also shown (dashed line).](image2)

![Fig. 3. Variations of $\Delta G_{\text{mix}}$ (kJ mol$^{-1}$) at 1000 K for MnO–MgO with composition, with and without relaxation are plotted. The difference between the two curves demonstrate the importance of atomic relaxation. All calculations are QLD.](image3)
In the absence of relaxation $\Delta G_{\text{mix}}$ vs. composition curves at 1000 K with and without relaxation. In the absence of relaxation $\Delta G_{\text{mix}}$ is positive for all compositions studied.

Monte Carlo simulations at a given temperature in the semigrand canonical ensemble yield the calculated variation of $\Delta H_{\text{Mg/Mn}}$ with composition. As in the Margules approximation, we write the excess (non-ideal) free energy as a third degree polynomial in the concentration. The chemical potential difference then consists of an ideal solution term and a second degree polynomial. The results for $\Delta u$ at each temperature were fitted to such a polynomial. Integration gives the variation of free energy with composition, and these $\Delta G_{\text{mix}}$ vs. composition curves are similar to those obtained using the optimized QLD energies in Fig. 3. There is also good agreement between $\Delta S_{\text{mix}}$ values obtained via the Monte Carlo free energy and enthalpy of mixing and those obtained from QLD. From the temperature variation of $\Delta G_{\text{mix}}$ it is straightforward to calculate the phase diagram, as in Ref. [13].

It is computationally much cheaper to optimize every configuration in the static limit, using lattice statics (LS) and replacing $G_k$ by $H_k$ (static) in Eqs. (1)-(4). The vibrational contribution to $H_k$ and the vibrational entropy $S_k$ are ignored. Only one set of runs over the composition scale is required for all temperatures. The curve labelled LS in Fig. 2 shows $\Delta S_{\text{mix}}$ calculated using this approximation. The difference between the QLD and LS values represents the vibrational contribution (denoted using the subscript ‘vib’). Neglecting effects due to thermal expansion, the LS values of $\Delta S_{\text{mix}}$ represent the configurational contribution to these quantities. The LS values of $\Delta S_{\text{mix}}$ are lower and smaller than the ideal entropy of mixing at all compositions. The configurational entropy of mixing is thus smaller than the ideal and the positive vibrational terms contribute to the entropy of mixing of CaO–MgO solid solutions.

For Py–Gr solid solutions we plot $\Delta H_{\text{mix}}$ at 1500 K and pressures from zero to 15 GPa in Fig. 4. These are all positive with a dip at lower pressures at a composition of $\approx 50:50$, possibly hinting at a preferential ordering of Ca$^{2+}$ and Mg$^{2+}$. Available experimental data [14] are also shown. These like the calculated values are positive and show similar asymmetry, with higher values for pyrope-rich garnets. Nevertheless quantitative agreement is rather poor. To some extent this can be related to large uncertainties in the calorimetric measurements. For example, three measurements of the enthalpy of pure end member pyrope differ by up to 2.4 kJ/mol [14]. Also shown in Fig. 4 is the analogous calculated $\Delta H_{\text{mix}}$ at 1500 K for Py–Alm at zero pressure. These values are all positive but much smaller than those for Py–Gr, as might be expected given the smaller size mismatch between Mg$^{2+}$ and Fe$^{2+}$. We suggest that an experimental re-examination of the enthalpy of mixing of Py–Gr and Py–Alm is highly desirable.

In Fig. 5, calculated excess volumes for Py–Gr are compared with experiment. $\Delta V_{\text{mix}}$ is large and positive, as observed experimentally [15,16]. These results are in better quantitative agreement with experiment than those for $\Delta H_{\text{mix}}$ although in general on the high side and possibly less asymmetric. It is important to bear in mind again that experimental uncertainties are large. In contrast to the results for Py–Gr, volumes of mixing along the Py–Alm join are small (between 0 and 0.05 cm$^3$/mol). This agrees with Ref. [17] which concludes experimental data are indistinguishable from ideal.

In order to investigate how the atomic scale behaviour of the garnet solid solutions influences the thermodynamic properties, we have studied the short-range...
Ca–Mg ordering in Py–Gr garnets. Previous experimental $^{29}$Si MAS MNR studies [18,19] together with computational results [20,21] concluded that the strongest cation interaction is that between dodecahedral sites linked via an edge-shared tetrahedron, i.e., between third nearest cation neighbours. We have monitored in our MCX simulations the nature of the third neighbour interactions in Py$_{50}$Gr$_{50}$ and Py$_{50}$Alm$_{50}$ as a function of temperature. Py–Alm behaves essentially as an ideal solution, with a random distribution of third neighbours. The Py–Gr solid solution is very different in that at low temperatures there are very few Mg–Mg (and Ca–Ca) third neighbour pairs. At higher pressures the number of Mg–Mg third nearest neighbour pairs increases in the Py–Gr solution. This is consistent with the different compressibilities of the Mg and Ca dodecahedral sites, with the Ca site more easily compressible and thus making the Mg and Ca sites more similar at higher pressures. This is also associated with the disappearance of the small dip in the composition variation of the enthalpies of mixing at higher pressures (Fig. 4) and the decrease of the enthalpy of mixing with increasing pressure.

3.3. Carbonates

Carbonates contribute a significant portion of the Earth’s crust but have proved experimentally challenging [22] making them an ideal candidate for simulation. Computationally modelling of carbonates has had mixed success; the use of Lippmann Diagrams [23,24] proved problematic. We have attempted to model dolomite, Ca$_x$Mg$_{1-x}$(CO$_3$)$_2$, has a hexagonal structure with planes of cations (Ca or Mg) separated by planes of carbonates.

Our calculations used a 72-cation unit cell (total atom number 360) over a range of compositions. All our calculations use LS and approximately 25,000 configurations. In Fig. 6, we present the calculated phase diagram of dolomite. The agreement with experiment is encouraging, with reproduction of all the main features. The main differences lie close to the end members and in large part are artefacts of the cell size used.

4. Final remarks

Solid solutions of ionic compounds have traditionally proved problematic for the theoretician. We have presented a range of methods for the simulation of such solid solutions, the accurate calculation of thermodynamic quantities of mixing, and also for the calculation of phase diagrams. No empirical data for the particular system under study are required. All the methods sample many configurations, explicitly considering different arrangements of ions, and allow for the local structural relaxation surrounding each cation. This relaxation is crucial. If ignored, the energy of exchange of any two ions is usually very high and all exchanges are rejected, thus sampling only one arrangement. All the methods include vibrational effects and are applicable over ranges of pressure and temperature. Disorder problems are often tackled by using a general Ising model, simplified by limiting interactions to a short range and a finite number of multi-site couplings. Such an approach is awkward to parameterize for ionic solids, where relaxation is crucial, and to apply over a range of pressures and temperatures. It is not readily generalised to less symmetric structures, to which we also wish to apply...
the general methodology outlined here. In our methodology, no assumptions are made as to the nature of the solid solution.

In particular, we have demonstrated how the rapid calculation of the free energy via quasiharmonic lattice dynamics can be used to calculate thermodynamic properties of solutions over wide ranges of pressure and temperature including $\Delta H_{\text{mix}}, \Delta S_{\text{mix}}$ and phase diagrams. Results compare well with those from Monte Carlo simulations in the semigrand canonical ensemble. Agreement is better at higher pressure [14] where internuclear distances are smaller and anharmonic contributions smaller. Quantum effects are included in the vibrational contributions at low temperatures. Calculated entropies of mixing include both configurational and vibrational contributions. For the latter we have seen when extrapolation from the point defect limit fails. The technique is limited by the accuracy of the quasiharmonic approximation, which breaks down with increasing amplitude of vibration and hence at high $T$, typically around two-thirds of the melting point for oxides.

The Monte Carlo and the configurational averaging methods each have their own strengths and advantages. Monte Carlo techniques are applicable to the solid at high temperatures and to melts [12]. The semigrand canonical ensemble is an attractive route to differences in chemical potential and consequent calculation of the free energy and the phase diagram. QLD is efficient in chemical potential and consequent calculation of canonical ensemble is an attractive route to differences in chemical potential and consequent calculation of the free energy via quasiharmonic lattice dynamics, Phys. Rev. B 56 (1997) 14380–14390.

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References


