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Convergent real-space cluster expansion for configurational disorder in ionic systems

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We present a rapidly converging, real-space expansion to compute the electrostatic energy of point-charge configurations on a fixed lattice. The rapid convergence is obtained by requiring that the expansion only reproduce well the configurations with energies below some cutoff energy. The convergence rate can be systematically varied by changing this cutoff. This expansion should prove useful for computations in which only low-energy states are required, such as free-energy and phase-diagram computations.

I. INTRODUCTION

Considerable interest exists in the first-principles computation of thermodynamic properties and phase diagrams of multicomponent materials. In many cases a lattice model is used to compute the thermodynamic potentials starting from a suitable model Hamiltonian. Although lattice models only explicitly account for configurational entropy, it has been shown that the effect of vibrational and electronic disorder can be included by course graining the full partition function to the partition function of a lattice model.[1] A lattice model can therefore be seen as the last step in integrating the partition function over all the degrees of freedom of a crystalline solid. For this reason, these models have become the cornerstone of the first-principles computation of thermodynamic properties in multicomponent crystalline materials. In this paper, we investigate the applicability of a real-space lattice model to an ionic system consisting of point changes and discuss the inherent problem of long-ranged Coulombic interactions.

To construct an effective lattice model Hamiltonian for a (pseudo)binary material, the energy is expanded in an orthogonal basis set of cluster functions:[2]

$$E(\sigma)=\sum_{\alpha} V_{\alpha} \prod_{i \in \alpha} \sigma_i \ . \tag{1}$$

In Eq. (1), σ_i is the occupation variable that takes on the value $+(-1)$ when site i is occupied by an A (B) species and the vector $\sigma=\{\sigma_1,\sigma_2,\sigma_3,\ldots\sigma_n\}$ labels the configuration of the complete system. The summation in Eq. (1) is over all figures α of lattice points, and the coefficients V_α are effective-cluster interactions (ECI). Typically, the ECI for a given system are determined by fitting a truncated form of the cluster expansion [Eq. (1)] to the energy of different ordered arrangements.[3-5] For metallic systems, these energies are often determined in the local-density approximation. Although only the ground-state energy is expanded as a function of configuration in Eq. (1), the effect of vibrations and electronic excitations could be included by expanding the relevant free energies.[6] In the model system we are going to study, these contributions are neglected.

The practical use of expansion (1) lies in the rapid convergence of the ECI with cluster size and separation distance between points in the cluster. There is some indication that in metallic systems this is the case when the elastic effects are treated properly.[4,7,8] Recent interest in applying the cluster expansion to ionic materials,[9-12] however, necessitates a careful reconsideration of the convergence of Eq. (1) in systems where strong electrostatic interactions are present. This is the purpose of this paper. We will compute the ECI for a model system in which fixed charges q_1 and q_2 are distributed on a static fcc lattice. As only charge-neutral systems will be investigated, the composition of the system is determined by the ratio q_1/q_2. For such a pairwise interacting system with no relaxations, the effective cluster interactions can be determined analytically, and the only nonzero interactions are effective-*pair* interactions given by

$$V_{ij}=\frac{(q_1-q_2)^2}{16\pi\epsilon_0 r_{ij}} \ , \tag{2}$$

where ϵ_0 is the free-space permittivity.

It is clear that the r^{-1} dependence of the ECI does not lead to a rapidly convergent expansion and therefore prohibits the use of a real-space cluster expansion to compute the free energy[13,14] of this system. This is an

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unusual situation, as in most systems the ECI converge much more rapidly than the bare atomic interactions. In this paper, we will however show that the r^{-1} dependence of the ECI is the result of the high-energy regions in configuration space and that much faster-converging expansions can be obtained by not requiring that the cluster expansion reproduce these regions with high energy.

II. PROCEDURE

To determine the ECI numerically, the electrostatic energy for 291 periodic configurations on the fcc lattice with $q_1 = -q_2 \equiv 1$ was computed by means of the Ewald summation technique.[15] The configurations have primitive unit-cell size ranging from 2 to 32 atoms per unit cell. The energies ranged from -1.6366 to 58.239 per ion in units of $q^2/8\pi\epsilon_0 d$ where d is the nearest-neighbor distance. These dimensionless units correspond to Madelung constants and will be used for all results in this paper. Values of the ECI were obtained by performing a least-squares fit to these energies with two different Hamiltonians: an intermediate-ranged Hamiltonian including the constant energy term (empty cluster interaction) and pairs up to the eighth-nearest-neighbor distance and a long-ranged Hamiltonian in which pairs extend up to the fifteenth-nearest-neighbor distance. The latter Hamiltonian contains 18 terms as there are two distinct ninth- and thirteenth-nearest-neighbor interactions on the fcc lattice. Since all structures have the same composition there is no need for a linear term in the Hamiltonian. For each Hamiltonian we will compare three sets of ECI: (a) the exact but truncated ECI [Eq. (2)], (b) the ECI obtained by fitting to all 291 structures, and (c) the ECI obtained by fitting to only the structures with energy below some cutoff value E_c. In most cases, E_c was chosen as zero, although there is no particular reason for this choice. With $E_c = 0$ there are 195 structures below the cutoff energy and 96 above. All ECI are normalized by the first-nearest-neighbor interaction (V_1).

III. RESULTS

Figure 1 shows the ECI for the intermediate ranged Hamiltonian (V_1 to V_8). The effective interactions obtained from fitting to the structures with energy below zero (broken line with open squares) converge much faster than the exact ECI (solid line with filled squares). The eighth-nearest-neighbor interaction in this fit is less than 1% of the nearest-neighbor interaction, as compared to 35% for the exact ECI. The slow convergence of the exact ECI is recovered when structures with large energy are also included in the fit (broken line with filled circles).

The quality of the fit for the rapidly converging cluster expansion is illustrated in Fig. 2. In this figure the energy computed from the cluster expansion is plotted versus the exact electrostatic energy. It can be observed that for the low-energy structures the fit is extremely good. The root-mean-square (rms) difference between the cluster expansion energy and the exact energy for the structures with energy below zero is 0.0403. It is remarkable that such a good fit can be obtained for 195 structures with only nine effective interactions. For the higher-energy structures, the cluster expansion energy starts to deviate significantly from the exact energy. Although Fig. 2 only shows energies up to 10, the complete set of structures included structures with energies up to 58.239. The predictive power of this fit can be tested by fitting to only a subset of the structural energies and comparing the predicted and exact energies for the structures left out of the fit. We performed this predictor test by fitting the Hamiltonian with first- through eighth-nearest-neighbor pair interactions to 88 of the 195 structures with energy below zero. The resulting ECI are very similar to those obtained in the full fit and were used to compute the energies of the other 87 structures with energy below zero. The rms error for these 87 structures was 0.0481, only slightly higher than the rms error obtained when the structures are included in the fit (0.0403). This indicates that we can predict the electrostatic energies for these structures with high accuracy without including them in the fit.

Figure 3 shows the value of the ECI obtained by fitting the long-ranged Hamiltonian (V_1 to V_{15}) to the electrostatic energies. Again the interactions obtained from fitting only the structures with energy below zero (broken line with open squares) converge much more rapidly than the exact solution (solid line with filled squares) or the in-

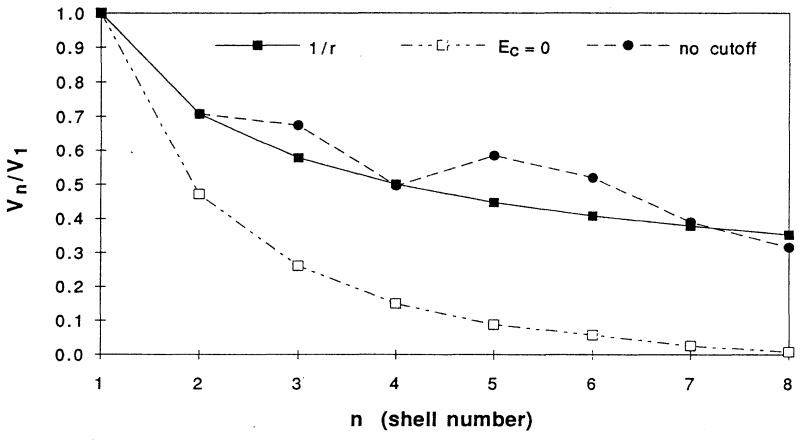

FIG. 1. Comparison between the exact ECI (filled squares with solid line) and the ECI obtained with two different fits (broken lines). The ECI obtained by fitting a Hamiltonian with first- to eighth-nearest-neighbor interactions to the energy of all 291 structures are shown in solid circles. The ECI indicated with squares were obtained by only fitting to the structures with energy below zero.

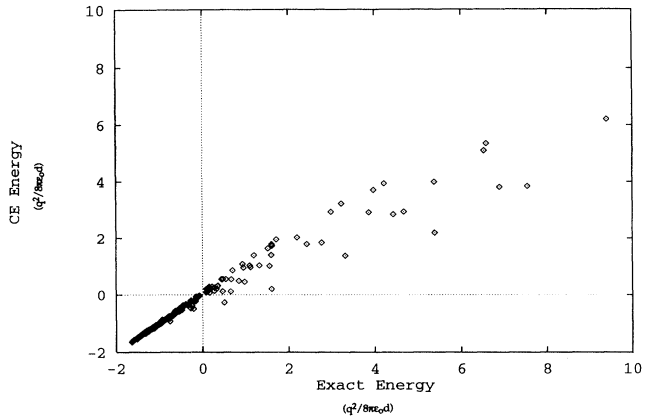

FIG. 2. Energies as reproduced by the rapidly converging cluster expansion (open squares in Fig. 1) versus exact electrostatic energies. The energies are in units of $q^2/8\pi\epsilon_0 d$ where d is the nearest-neighbor distance.

teractions obtained from fitting all the structures (broken line with solid circles). The rms difference between the exact and fitted energies for the low-energy structures has now decreased to 0.0157.

Figures 1 and 3 show that the ECI converge faster when only configurations with energy below a cutoff (E_c) are included in the fit. The effect of varying E_c is systematic: The convergence of the ECI can be accelerated or slowed by, respectively, bringing the cutoff energy to lower or higher values. This is demonstrated in Fig. 4 which shows, as a function of the energy cutoff, how many interaction shells have to be included so that the last ECI has decayed to 1% of V_1.

IV. DISCUSSION

Although the exact ECI in this system decay only as r^{-1}, it is clear that an extremely good fit to the low-energy states can be obtained with a rapidly decaying set of effective-pair interactions. The change in the value of ECI as the interaction range in the Hamiltonian is extended from the eighth- to the fifteenth-nearest-neighbor distance, is to be expected here since we are not obtaining the exact ECI. In all cases, however, the ECI remain repulsive and convex decaying with distance, a signature of electrostatic interactions. The convergence rate of the ECI can be systematically varied by changing the cutoff energy.

The fact that a rapidly converging cluster expansion can be obtained should prove to be extremely useful to predict ground states and phase diagrams of ionic systems with real-space models. In these cases, the system will only sample the low-energy states so that a rapidly converging expansion can be used without sacrificing accuracy. In this respect, it is important to note that the high-energy structures that were not used in the fit are still predicted to have a high energy, so that they do not interfere with the low-energy states: For the long-ranged Hamiltonian ($V_1 - V_{15}$) all configurations with exact energy above the cutoff were predicted to be above the cutoff by the cluster expansion. With the intermediate-ranged Hamiltonian, only one structure with energy above the cutoff was predicted to be below the cutoff by the cluster expansion.

The cutoff energy will determine for what range of energies the cluster expansion is valid. In our example, the cutoff energy was 1.6366 above the ground-state energy [in units of $(q_1 - q_2)^2/32\pi\epsilon_0 d$]. In an $(A^{+2})_2(B^{+3}B^{+5})O_6$ perovskite, for example, the distance between the B ions is typically around 0.4 nm so that this energy cutoff corresponds to an electrostatic energy of 1.85 eV above the ground-state energy. It seems therefore unlikely that a system in equilibrium will ever sample states that are not well reproduced by the fast decaying cluster expansion.

The rapid decay of the electrostatic ECI fitted to the low-energy part of configuration space can be understood from the requirement of local charge neutrality in structures with low energy. Low-energy structures do not have long-ranged charge imbalance, implying that, *on the average,* ions do not effectively interact with their environment outside some radius of charge neutrality. Of course, ions interact individually over much larger distances, but on average, the electrostatic field from the region far away does not depend on the details of the ar-

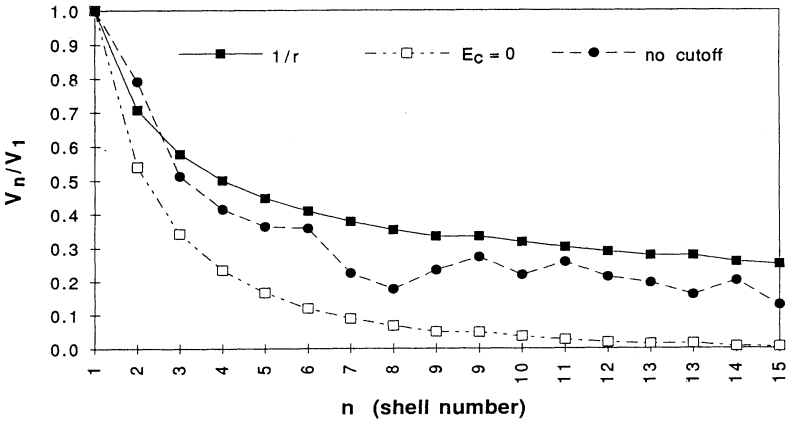

FIG. 3. Similar to Fig. 1, but for a Hamiltonian with first- through fifteenth-nearest-neighbor interactions.

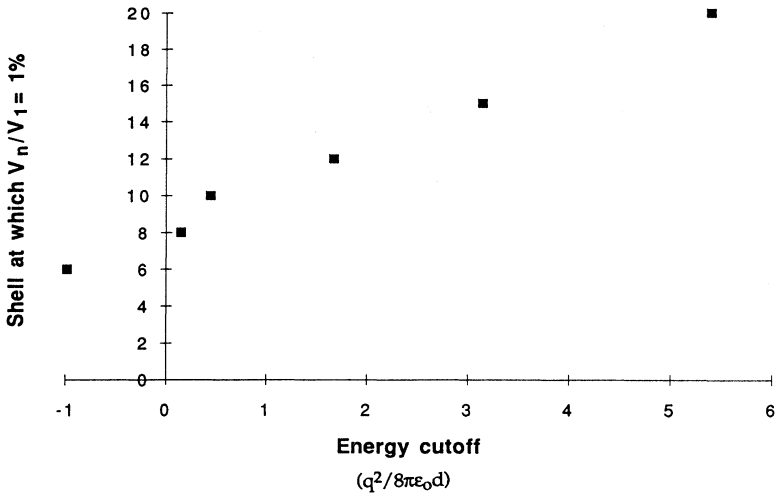

FIG. 4. Shell at which the effective-pair interaction has decayed to 1% of the nearest-neighbor interaction as a function of the cutoff energy.

rangement in that region, provided the charge is constant there. Only in structures in which there are large charged regions will long-ranged effective interaction be necessary. In the latter case, the short-range correlation functions are not affected by the charge imbalance, hence a short-range cluster expansion cannot reproduce the electrostatic energy in those cases.

Our results parallel earlier observations that the radial distribution functions of ionic liquids can be reproduced by model simulations with relatively short-ranged interactions between the ions.[16,17] It thus seems to be fairly general that low-energy states in ionic systems may be modeled with short-ranged interactions. Some light can be shed on the origin of these phenomena by considering the well-known Ewald summation method. In the Ewald technique the electrostatic energy is divided into three terms: $E_{\text{tot}}=E_c+E_r+E_k$, where E_c is a constant term,

$$E_c=-\frac{\alpha}{\sqrt{\pi}}\sum_i q_i^2 , \tag{3a}$$

E_r is a real-space pairwise term,

$$E_r=\frac{1}{2}\sum_{i,j} q_i q_j \frac{\operatorname{erfc}(\alpha r)}{r} , \tag{3b}$$

and E_k is summed in k space,

$$E_k=-\sum_{\mathbf{k}} S(\mathbf{k})\frac{1}{|\mathbf{k}|^2}\exp\left[\frac{-|\mathbf{k}|^2}{4\alpha^2}\right] . \tag{3c}$$

$S(k)$ is the Fourier transform of the set of point charges. For a large-enough value of the parameter α, the real-space contribution is rapidly convergent. Since E_k is dominated by the structure factor intensity near the origin, its magnitude will be small for structures with no long-wavelength charge imbalance. For these structures, E_k can be neglected and the energy can be obtained in real space with a limited interaction range. We verified this numerically. Using $\alpha=1.41$ divided by the nearest-neighbor distance, we found that for most of the structures with $E_{\text{tot}}<0$, E_k was between -0.05 and 0.05. For structures with $E_{\text{tot}}>5$, E_k becomes of the same order of magnitude as the total energy. The technique of neglecting E_k in the Ewald sum has been used by some researchers to accelerate molecular-dynamics simulations of ionic systems.[18,19] To test the accuracy of this approximation and compare it to the cluster expansion we computed the formation energies for all 291 structures using only the terms E_c and E_r, with the latter term truncated after the fifteenth-nearest-neighbor distance. We chose α equal to 0.475 as this gives the same ratio for V_{15}/V_1 as for the fitted expansion in Fig. 3. Although this approximation resulted in much more accurate formation energies than can be obtained with the truncated $1/r$ interaction, the rms error for the structures with $E<0$, was a factor 2.5 larger than with the fitted Hamiltonian.

Since the exact ECI for our model system decay as $1/r$, all the expansions presented here will only be accurate in a limited region of configuration space. In less ionic systems, both charge transfer and screening can reduce the energy of high-energy configurations so that it can be expected that even the *exact* ECI in these materials will decay faster than r^{-1}. In metals, for example, atoms will typically only transfer charge from atoms that are in close proximity so that configurations with long-range charge imbalances will never occur. Convergence of the ECI for these systems was already demonstrated by Magri, Wei, and Zunger.[20] In their model system, the charge on an atom was variable and proportional to the number of unlike atoms in the nearest-neighbor shell, ensuring that an isolated charge is screened within the nearest-neighbor shell. This charge-transfer mechanism prevents states in which like atoms are clustered together to have a very high energy, and therefore leads to a rapidly converging expansion. Although first-principles electron-density calculations have confirmed that this simple charge-transfer model is realistic for metallic alloys,[21,22] its applicability to strongly ionic systems such as oxides or halides has not been verified. However, our work demonstrates, that even if these energy lowering mechanisms do not occur, a convergent cluster expansion can be constructed for the important low-energy part of configuration space. One can thus be confident that ionic systems can be modeled with short-ranged real-space cluster expansions.

V. CONCLUSION

We have shown that even in a rigid electrostatic system that undergoes no screening or charge transfer, a rapidly converging cluster expansion can be constructed that accurately reproduces the low-energy configurations. This expansion can be constructed by fitting the ECI to a set of low-energy structures. The convergence rate of the ECI increases as less high-energy states are used in the fit. When including configurations with very high energy in the ECI fit, the exact r^{-1} behavior can be approached. It is thus clear that short-ranged real-space cluster expansion can be used for applications where only low-energy configurations are required, such as phase-diagram and free-energy computations. Although our model consisted of ions on a rigid lattice, our conclusions should remain valid when relaxations are allowed.

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