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General relations between many-body potentials and cluster expansions in multicomponent systems

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Abstract

We demonstrate that the energy of a system of atoms can be uniquely evaluated using a series of structure independent, perfectly transferable many-body potentials. This allows one to compare empirical energy parametrizations on the basis of the behaviours of their potential expansions. It is shown how the representations of the energy using many-body potentials, which focuses on the positional degrees of freedom, and the conventional cluster expansion method, which focuses on the ordering degrees of freedom in a multicomponent lattice system, can be merged into a generalized cluster expansion.

1. Introduction

On the basis of the reasoning of Born and Oppenheimer [1] in 1927, many quantum mechanical calculations of the electronic structure of a system of atoms treat the nuclei as classical point masses. The energy of a system of atoms is adiabatically parametrized by the positions of the nuclei. Accurate methods exist for calculating the energy of a few atoms in some configurations; an overall evaluation of the energy hypersurface, however, is impossible and, even if it was carried out, one would not gain physical insight. Due to the ever growing interest in mesoscopic systems, e.g., for the development of advanced materials with applications in nanotechnology, a wealth of approximations to the many-body problem have been developed [2–4]. Most such approximations are designed to describe certain aspects of interest of a given system. The different approaches used to approximate the adiabatic energy hypersurface may be classified according to three different routes. The first route decomposes the total energy in many-body potentials, i.e., pair, three-body, four-body, . . ., N-body potentials. According to the classification of Carlsson [2], these many-body potentials can also be denoted as cluster potentials. There are two problems associated with many-body potentials developed along these lines. First, up to now there has been no unique prescription for constructing for a given system a many-body potential which is perfectly transferable, i.e., which can be used for each conceivable configuration of the system, and to the best of our

knowledge it has not been rigorously proven that such a unique prescription exists. It is one of the main objectives of the present paper to give an explicit prescription for constructing perfectly transferable many-body potentials. Second, the many-body potentials in general exhibit a rather slow convergence. Therefore, a second route is replacing the many-body potentials by effective potentials that show a faster convergence. Following the classification of Carlsson [2] we refer to this large class of potentials as cluster functionals. Commonly, cluster functionals represent the energy as a sum of a pair interaction term and a rest term. The rest term is formally written as the sum of contributions of single atoms; each of the contributions of a single atom, however, depends on the surroundings of the atom as it is a function of atom pairs, triplets, ... As will be seen, the various contributions to the rest term can in some sense be conceived as clever partial summations of the many-body potentials, and therefore the cluster functionals have an improved convergence behaviour. Again no clear-cut prescription for constructing cluster functionals exists; they are often constructed according to physical intuition and therefore their transferability is often limited. A second problem is that there already exist a great manifold of different cluster functionals, and there is no systematic way to compare various cluster functionals in an objective manner. It will be the second objective of the present paper to demonstrate that by using our definition of perfectly transferable many-body potentials we are in the position to perform such a systematic and objective comparison.

A third route to the evaluation of the energy is the cluster expansion method which in the past has been used mainly for systems where the atoms are fixed on certain lattice positions and where there are only chemical degrees of freedom provided by different possible arrangements of the various kinds of atoms on the fixed sites. In the cluster expansion method the total energy is represented as a sum of contributions over all conceivable clusters in the system. The cluster expansion method was introduced by Sanchez *et al* [5]. Extensive work was also done by Zunger *et al* [6] in an effort to handle the effect of local relaxations and long-range elastic interactions. For practical calculations the cluster expansion has to be terminated at a maximum cluster, and it is not clear which clusters have to be kept in such a terminated cluster expansion. We will show that for systems for which a reasonable cluster functional exists, we can preselect the relevant clusters of the cluster expansion by using the expansion in transferable many-body potentials. Furthermore, we will show how the many-body potential expansion, which often emphasizes the positional degrees of freedom, can be merged with the cluster expansion method, which was mainly used for chemical degrees of freedom, resulting in a cluster expansion not confined to lattices.

The outline of this paper is as follows. In section 2 we show how a general potential expansion can be used as a natural framework for the derivation of analytical approximations to the many-body problem. Within this framework the various approaches to the many-body problem can be judged by their physical bases as well as their transferability to different configurations, e.g., bulk, surfaces and the gas phase. We will demonstrate the usefulness of the approach in section 4 with two simple but popular analytical potentials. In section 3 the foundations developed in the first section of this paper are used to establish a direct link between the energy hypersurface, represented in terms of the potential expansion, and the thermodynamic properties of multicomponent compounds, e.g., the energy of formation, represented in terms of the cluster expansion. Such a link should allow for a faster theoretical assessment of the phase diagram of alloys and related temperature dependent properties.

2. Potential expansion

In this section we show that a general potential expansion can be used as a common basis that allows one to compare the various, very different approaches to the many-body problem.

A unified treatment of the energy hypersurface of a crystal then allows one to extract the cluster expansion coefficients as local quantities in section 3.

We denote the total energy of a M particle system using

$$E_M = E_M(X_1, X_2, \ldots, X_M), \tag{1}$$

where the position $\boldsymbol{R}_n$ of atom n was grouped together with the species of atom n denoted by an integer σ_n, $X_n = \{\boldsymbol{R}_n, \sigma_n\}$.[3] As the order of labelling the M atoms is arbitrary, the form of E_M must be such that E_M is invariant when two labels are exchanged, $X_i \leftrightarrow X_j$:

$$E_M(X_1, \ldots, X_i, \ldots, X_j, \ldots, X_M) = E_M(X_1, \ldots, X_j, \ldots, X_i, \ldots, X_M). \tag{2}$$

Hence E_M is symmetric with respect to $X_i \leftrightarrow X_j$. We start from the representation of the energy E_M as an expansion in a series of N-body interaction potentials $V^{(N)}$ via[4]

$$E_M = E_M(X_1, X_2, \ldots, X_M) = \sum_{N=0}^{M} E^{(N)}(X_1, X_2, \ldots, X_M), \tag{3}$$

$$E^{(N)} = \frac{1}{N!} \sum_{m_1}^{M} \sum_{m_2}^{M} \cdots \sum_{m_N}^{M} V^{(N)}(X_{m_1}, X_{m_2}, \ldots, X_{m_N}), \tag{4}$$

where the summation is carried out over pairwise different indices. It is generally assumed [2, 3] (but to the best knowledge of the authors, nowhere rigorously proved) that the potentials $V^{(N)}$ can be chosen as being independent of the environment in which the atoms $\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_N$ are embedded, so that they are structure independent and therefore transferable to any atomic configuration, including all solid and liquid configurations formed by the atoms. The inversion of equations (3), (4) is straightforward for small values of M [2]. For example, the pair potential $V^{(2)}$ is calculated from E_2 and E_1 as

$$E_2(X_1, X_2) = \tfrac{1}{2}\left(V^{(2)}(X_1, X_2) + V^{(2)}(X_2, X_1)\right) + V^{(1)}(X_1) + V^{(1)}(X_2) + V^{(0)}$$

$$\stackrel{\text{Eq. (2)}}{=} V^{(2)}(X_1, X_2) + E_1(X_1) + E_1(X_2) - E_0, \tag{5}$$

where we made use of

$$E_1(X_1) = V^{(1)}(X_1) + V^{(0)}. \tag{6}$$

The explicit calculation of $V^{(N)}$ for general N becomes tedious to carry out along these lines. In general, equations (3), (4) can be inverted via Möbius inversion [7]. For this transformation we consider all isolated L-atom clusters contained in an N-atom cluster. We denote the energies of the L-atom clusters using $L = 1, 2, \ldots, N$ by E_L. The Möbius inversion of equations (3), (4) then reads

$$V^{(N)}(X_1, X_2, \ldots, X_N) = \sum_{L=0}^{N} \frac{(-1)^{N-L}}{L!} \sum_{m_1}^{N} \sum_{m_2}^{N} \cdots \sum_{m_L}^{N} E_L(X_{m_1}, X_{m_2}, \ldots, X_{m_L}). \tag{7}$$

Equation (7) constitutes a unique definition of N-body potentials $V^{(N)}$ which are structure independent because this equation does not carry any information about the environment of

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[3] This definition for $X_n = \{\boldsymbol{R}_n, \sigma_n\}$ will be most useful in accessing transferable potentials that are independent of their surroundings. In the context of phase diagram calculations of multicomponent alloys one is often only interested in small displacements of the atom positions with respect to given lattice sites $\{\boldsymbol{R}_n^0\}$. In this case we define $X_n = \{\boldsymbol{R}_n - \boldsymbol{R}_n^0, \sigma_n\}$. By using this latter definition we arrive at potentials which are adapted to describe, e.g., phonons or small relaxations, but we lose the perfect transferability of the potentials.

[4] It is sometimes argued [2] that a potential expansion converges only slowly with respect to the order of the potentials and is thus impractical for use in molecular dynamics simulations. We acknowledge this point; however, we focus in this paper on the comparison and the transferability of various potentials, where equation (7) turns out to be the only possible systematic definition with such an objective.

the atom clusters. Once the potentials $V^{(N)}$ have been constructed, they can be used to calculate the energy $E^{(M)}$ according to equations (3), (4) for any gaseous, liquid or solid state of the material, i.e., these potentials $V^{(N)}$ are perfectly transferable by construction.

Equation (7) also shows that the potentials are uniquely defined from the energies of isolated subclusters. Thus in principle the potentials $V^{(N)}$ can be determined from total energy *ab initio* calculations for isolated clusters of $L = 1, \ldots, N$ atoms without further approximation.

3. Relation to the cluster expansion method

In the statistical mechanics of multicomponent alloys one commonly simplifies the calculation of phase diagrams by introducing a lattice. The position of an atom $\boldsymbol{R}_i$ in this system is assigned to a lattice site $\boldsymbol{R}_i^0$. The remaining degree of freedom is the occupation of each lattice site by one of the P different kinds of atoms present in the system. Each atomic species is denoted with an integer value $\pm p, \pm(p-1), \ldots, \pm 1, (0)$ (where 0 is included if $P = 2p+1$). The occupation of lattice site i is characterized by $\sigma_i \in \{\pm p, \pm(p-1), \ldots, \pm 1, (0)\}$. The configuration of the lattice is given by the occupation vector $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \ldots \sigma_M)$. An orthonormal and complete set of basis functions $\Theta_v(\sigma_i)$ with $v = 0, 1, 2, \ldots, (P-1)$ and $\Theta_0(\sigma_i) = 1$ is introduced (e.g., the first P Chebyshev polynomials [5]):

$$\sum_{\sigma} \Theta_{v_1}(\sigma) \Theta_{v_2}(\sigma) = P \delta_{v_1 v_2}, \tag{8}$$

$$\sum_{v=0}^{P-1} \Theta_v(\sigma_1) \Theta_v(\sigma_2) = P \delta_{\sigma_1 \sigma_2}, \tag{9}$$

with $\sigma_1, \sigma_2 \in \{\pm p, \pm(p-1), \ldots, \pm 1, (0)\}$.

The basis for the whole configurational space of M lattice sites is given by the direct product of the basis functions for all sites:

$$\Phi_{\alpha v}^{(M)}(\boldsymbol{\sigma}) = \Theta_{v_1}(\sigma_1) \Theta_{v_2}(\sigma_2) \cdots \Theta_{v_M}(\sigma_M). \tag{10}$$

The lattice sites are grouped in clusters $\alpha_K = \{m_1, m_2, \ldots, m_K\}$ with $K \leqslant M$ and $m_1 < m_2 < \cdots < m_K$; to each of the clusters α_K one assigns the vectors $v_K = (v_1, v_2, \ldots, v_K)$ with $v_l \in \{1, 2, \ldots, (P-1)\}$, where the various v_l are not necessarily pairwise distinct. Having established a complete basis in configurational space, the energy of any conceivable configuration $\boldsymbol{\sigma}$ can be represented as a sum of contributions arising from all possible clusters α_K [5]:

$$E(\boldsymbol{\sigma}) = J_0 + \sum_{K=1}^{M} \sum_{\alpha_K} \sum_{v_K} J_{\alpha v}^{(K)} \Phi_{\alpha v}^{(K)}(\boldsymbol{\sigma}). \tag{11}$$

The cluster expansion coefficients $J_{\alpha v}^{(K)}$ are obtained by projecting the total energy onto the corresponding cluster function:

$$J_{\alpha v}^{(K)} = \langle E(\boldsymbol{\sigma}) | \Phi_{\alpha v}^{(K)}(\boldsymbol{\sigma}) \rangle, \tag{12}$$

where the scalar product of two configuration dependent functions $f(\boldsymbol{\sigma}), g(\boldsymbol{\sigma})$ is defined as

$$\langle f(\boldsymbol{\sigma}) | g(\boldsymbol{\sigma}) \rangle = \frac{1}{P^M} \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_M} f(\boldsymbol{\sigma}) \cdot g(\boldsymbol{\sigma}). \tag{13}$$

The projection formula (12) can be decomposed into a part involving the positions of a given cluster α_K and a part that is independent of the occupation σ_{α_K} of cluster α_K (denoted by $M - \alpha_K$) [10]:

$$J_{\alpha v}^{(K)} = \frac{1}{P^K} \sum_{\sigma_{\alpha_K}} \Theta_{v_{m_1}}(\sigma_{m_1}) \Theta_{v_{m_2}}(\sigma_{m_2}) \cdots \Theta_{v_{m_K}}(\sigma_{\alpha_{m_K}}) W_{\alpha_K}, \tag{14}$$

with

$$W_{\alpha_K} = \frac{1}{P^{M-K}} \sum_{\sigma_{M-\alpha_K}} E(\alpha, M - \alpha_K). \tag{15}$$

The cluster expansion coefficients $J_{\alpha v}^{(K)}$ depend neither on the composition nor on the configuration σ of the system. The inversion of equation (11) is carried out routinely for simple lattices, such as fcc and bcc ones. Often, for this purpose, the energy of a set of configurations $\sigma^{(1)}, \sigma^{(2)}, \ldots, \sigma^{(N)}$ is calculated *ab initio* and then used to numerically extract the expansion coefficients $J_{\alpha v}^{(K)}$. This approach, however, becomes tedious for multicomponent alloys or in restricted geometries, e.g., for surfaces, where many expansion coefficients are expected to be different from zero and cannot be related by symmetry. The reason for the increased effort required to calculate the full set of expansion coefficients in complicated geometries compared to one-atom unit cells lies in the global projection of equation (12): the whole system has to be taken into account in order to be able to extract the value of an expansion coefficient of a local cluster.

The representations of the energy in terms of N-body potentials $V^{(N)}$, equations (3), (4), and according to equation (11) have been considered [2] as two fundamentally distinct energy representations which focus on the positional and the ordering degrees of freedom. It is another objective of the present paper to show how the total energy of a system represented by uniquely defined N-body potentials can be cast in terms of the cluster expansion method. We thereby arrive at an energy representation for arbitrary chemical and positional degrees of freedom which has the form of equation (11). This allows us to calculate the expansion coefficients $J_{\alpha v}^{(K)}$ from local N-body potentials $V^{(N)}$, in contrast to the global inversion required in equation (12).

To do this we rewrite the contribution $E^{(N)}$ of all N-body potentials to the total energy of an M-atom system as defined via equations (3), (4) in the following way:

$$E^{(N)} = \frac{1}{N!} \sum_{m_1}^{M} \sum_{m_2}^{M} \cdots \sum_{m_N}^{M} V^{(N)}(X_{m_1}, X_{m_2}, \ldots, X_{m_N})$$

$$= \frac{1}{N!} \sum_{m_1} \sum_{m_2} \cdots \sum_{m_N} V^{(N)}\left(\boldsymbol{R}_{m_1}, \sigma_{m_1}; \ldots; \boldsymbol{R}_{m_N}, \sigma_{m_N}\right)$$

$$= \frac{1}{N!} \sum_{m_1 m_2, \ldots, m_N} \sum_{i_1 i_2, \ldots, i_N} V^{(N)}\left(\boldsymbol{R}_{m_1}, i_1; \ldots; \boldsymbol{R}_{m_N}, i_N\right) \prod_{l=1}^{N} \delta_{i_l, \sigma_{m_l}}. \tag{16}$$

Please note that m_i now labels not a lattice site (as in the conventional CE) but an arbitrary site in space. Inserting for $\delta_{i_l, \sigma_{m_l}}$ the completeness relation (9), one finds that the potential $V^{(N)}$ contributes to the expansion coefficient of the cluster α_K ($K \leqslant N$) in an effective way:

$$V_{\binom{N}{K}}^{(N)}(\boldsymbol{R}_1, \sigma_1; \ldots; \boldsymbol{R}_K, \sigma_K) = \frac{1}{P^{N-K}} \frac{1}{(N-K)!}$$

$$\times \sum_{m_{K+1}, \ldots, m_N} \sum_{\sigma_{K+1}, \ldots, \sigma_N} V^{(N)}(\boldsymbol{R}_1, \sigma_1; \ldots; \boldsymbol{R}_{m_N}, \sigma_{m_N}). \tag{17}$$

The effective potentials $V\binom{N}{K}$ are analogous to the effective energies W_α defined in equation (15); however, the effective potentials $V\binom{N}{K}$ are obtained from local potentials $V^{(N)}$ whereas for the construction of W_α the energy for the whole crystal needs to be evaluated.

The occupation averaged potential $V\binom{N}{K}$ is then projected onto the basis of configurational space with $\alpha_K = \{\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_K\}$:

$$J_{\alpha\nu}^{\binom{N}{K}} = \frac{1}{P^K} \sum_{\sigma_1 \ldots \sigma_K} \Phi_{\alpha\nu}^{(K)}(\sigma_1, \ldots, \sigma_K) V\binom{N}{K}(\boldsymbol{R}_1, \sigma_1; \ldots; \boldsymbol{R}_K, \sigma_K), \tag{18}$$

and the total cluster expansion coefficient is calculated as the sum of all contributions of the potentials:

$$J_{\alpha\nu}^{(K)} = \sum_{N=K}^{M} J_{\alpha\nu}^{\binom{N}{K}}. \tag{19}$$

It becomes obvious from equation (19) that only potentials $V^{(N)}$ with $N \geqslant K$ contribute to the expansion coefficients $J_{\alpha\nu}^{(K)}$. By the contributions with $N > K$ the cluster α_K is embedded into its 'grey' averaged surroundings as the sum in equation (17) runs over all possible occupations of all positions not contained in α_K.

In addition to the aesthetic value of having a link between the N-body potential representation and the CE, equation (19) is also of practical value. Because in any calculation only a finite number of clusters α_N can be involved in the CE, there is always an open question (which so far has been solved by trial and error) of which of the various possible clusters are the most essential ones. Provided that there already exists a reasonably reliable empirical N-body functional for the system under consideration, we can determine via equation (7) the N-body potential and then via equation (19) the expansion coefficients $J_{\alpha\nu}^{(K)}$. We can thus make a first guess for the cluster expansion coefficients $J_{\alpha\nu}^{(K)}$ which must be used in the construction of a CE on a lattice system from the energies of reference configurations calculated using *ab initio* electron theory.

Often, due to the size mismatch of the constituents of an alloy, the atoms do not take their ideal lattice positions, but relax into a lower energy state where the atomic positions are displaced from their ideal lattice sites. The relaxation energy of a given configuration is defined as the energy difference between the energy of the configuration of atoms on an ideal undistorted lattice and the energy of the configurations with the whole crystal's atomic positions locally relaxed. For many systems, the calculation of phase diagrams requires one to take into account local relaxations in the cluster expansion coefficients [6]. Equation (19) allows one to calculate the energetic contribution of relaxations to the cluster expansion coefficients on a lattice from the many-body potential expansion.

4. Comparison of empirical potentials

As we have established a one-to-one correspondence between the energy of a system and its potential expansion, we must accept that the convergence of equations (3), (4) with respect to the order N is determined solely by the structure of the energy function E_M. On this footing, frequently used approaches such as that based on so-called cluster functionals [2], which may be conceived of as rapidly converging but are in general limited transferable energy representations in terms of effective N-body interactions, are now regarded as physically motivated partial summations of special branches of the total energy. We illustrate this viewpoint with two examples. The embedded atom method [8] approximates the total energy as a function of

superimposed atomic charge densities ρ_{ij} and a repulsive pair potential $V^{(2,\text{rep})}$:

$$E = \sum_i F\left(\sum_j \rho_{ij}\right) + \tfrac{1}{2}\sum_{ij} V_{ij}^{(2,\text{rep})}. \tag{20}$$

Hence, the many-body potentials are related to the densities ρ_{ij} by

$$\sum_j^M \rho_{ij} = F^{-1}\left(\frac{1}{2}\sum_j^M \left(V_{ij}^{(2)} - V_{ij}^{(2,\text{rep})}\right) + \frac{1}{3!}\sum_{jk}^M V_{ijk}^{(3)} + \cdots\right). \tag{21}$$

In order for the embedded atom method to yield a truly transferable description of the energy, equation (21) has to hold for arbitrary values of M. The same requirement holds for effective pair potential approaches, where the total energy is written as

$$E = \tfrac{1}{2}\sum_{ij} f_{ij} V_{ij}^{(2,0)} + \tfrac{1}{2}\sum_{ij} V_{ij}^{(2,\text{rep})}. \tag{22}$$

The screening function f_{ij} in general has to fulfil

$$f_{ij} = \frac{V_{ij}^{(2)} - V_{ij}^{(2,\text{rep})}}{V_{ij}^{(2,0)}} + \frac{2}{3!}\frac{\sum_k^M V_{ijk}^{(3)}}{V_{ij}^{(2,0)}} + \cdots \tag{23}$$

for arbitrary values of M. A frequently used simple approximation to f_{ij} in covalent materials assumes an exponential decay of the screening function [9]:

$$f_{ij} = \exp\left(-B\sum_k g_{ijk}\right). \tag{24}$$

To obtain more compact notation, we furthermore assume $g_{ijk} = g_{jik}$. Potential expansion with equation (7) and $S_{ijk} = \exp(-Bg_{ijk}) - 1$ gives

$$\begin{aligned}
V^{(1)} &= V^{(0)} = 0,\\
V^{(2)}(1,2) &= V_{12}^{(2,0)} + V_{12}^{(2,\text{rep})},\\
V^{(3)}(1,2,3) &= S_{123} V_{12}^{(2,0)} + S_{231} V_{23}^{(2,0)} + S_{312} V_{31}^{(2,0)},\\
V^{(4)}(1,2,3,4) &= S_{124} S_{123} V_{12}^{(2,0)} + S_{134} S_{132} V_{13}^{(2,0)} + \cdots,\\
V^{(5)}(1,2,3,4,5) &= S_{125} S_{124} S_{123} V_{12}^{(2,0)} + \cdots,\\
V^{(6)}(1,2,3,4,5,6) &= S_{126} S_{125} S_{124} S_{123} V_{12}^{(2,0)} + \cdots,\\
&\vdots
\end{aligned} \tag{25}$$

Equation (25) shows that the exponential form of f_{ij} results in an algebraic decay of $V^{(N)}$ with respect to the screening S. For most practical calculations one assumes $S_{ijk} = 0$ when the distances between any two of the coordinates $\boldsymbol{R}_i$, $\boldsymbol{R}_j$, $\boldsymbol{R}_k$ are larger than a nearest-neighbour distance. Then the energy of the effective pair potential method for a fcc crystal is fully mapped by potentials $V^{(N)}$ with $N \leqslant 6$.

The situation is different for the embedded atom method. We assume [11]

$$F(x) = f_0 x \ln x. \tag{26}$$

Potential expansion using equation (7) yields

$$
\begin{aligned}
V^{(1)} &= V^{(0)} = 0, \\
V^{(2)}(1,2) &= f_0\big(\rho_{12}\ln(\rho_{12}) + f_0\rho_{21}\ln(\rho_{21})\big) + V_{12}^{(2,\mathrm{rep})}, \\
V^{(3)}(1,2,3) &= -f_0\left(\rho_{12}\ln\left(\frac{\rho_{12}}{\rho_{123}}\right) + \rho_{13}\ln\left(\frac{\rho_{13}}{\rho_{132}}\right) + \cdots\right), \\
V^{(4)}(1,2,3,4) &= f_0\left(\rho_{12}\ln\left(\frac{\rho_{12}\rho_{1234}}{\rho_{123}\rho_{124}}\right) + \cdots\right), \\
V^{(5)}(1,2,3,4,5) &= -f_0\left(\rho_{12}\ln\left(\frac{\rho_{12}\ \rho_{1234}\rho_{1235}\rho_{1245}}{\rho_{123}\rho_{124}\rho_{125}\ \rho_{12345}}\right) + \cdots\right), \\
&\;\;\vdots
\end{aligned}
\tag{27}
$$

with

$$
\rho_{i,m_1,\ldots,m_N} = \sum_{j=1}^{N}\rho_{i,m_j}.
\tag{28}
$$

We note that the embedded atom method can be cast as an effective pair potential scheme according to equations (22), (23). Second, equation (26) induces a logarithmic decay of the potentials $V^{(N)}$. If we assume $\rho_{ij} = 0$ when the distances between the coordinates $\boldsymbol{R}_i, \boldsymbol{R}_j$ are larger than a nearest-neighbour distance, in a fcc lattice a potential expansion requires potentials $V^{(N)}$ with $N \leqslant 13$ in order to fully map the energy of the embedded atom method. This reflects the physical idea behind the embedded atom method: the energy of an atom is calculated from the energy of the electron density provided by neighbouring atoms. Obviously this picture is better suited for the description of a metal. Thus we can decide via the expansion in N-body potentials for any given form of an energy hypersurface whether it is more appropriate for the description of a covalent system (then the decay of the $V^{(N)}$ is more algebraic-like) or a metallic system (then it is more logarithmic-like). A systematic investigation of more of the currently used cluster functionals along these lines would certainly be very interesting.

Apart from providing a general framework for a systematic analysis of already existing cluster functionals, equation (7) also defines a way to obtain perfectly transferable N-body potentials by *ab initio* calculations [2]. To do this, the energies E_L of isolated L-atom clusters have to be calculated using *ab initio* electron theory for a variety of positions; then the data have to be interpolated by means of appropriately chosen functions. This procedure is certainly extremely time-consuming and the convergence of the so-obtained N-body potential expansion may be slow; however, it yields perfectly transferable potentials. To judge the transferability and accuracy of the potentials in equations (25) and (27), only a few first-principles calculations are required: if a potential fails to correctly predict the energy of, e.g., a pair of atoms at a given distance, in a small cluster, at a surface or in bulk material, it is not transferable.

We calculated the pair potential contribution $J_{(2)}^{(2)}$ in NiAl explicitly using *ab initio* electron theory; see figure 1. Comparison to the nearest-neighbour expansion coefficient $J^{(2)}$ for a fcc lattice in NiAl [13] shows that many-body interactions screen the contribution of the pair potential to the pair expansion coefficient by around 70%, which emphasizes the importance of many-body interactions.

5. Conclusions

In the present paper, the following were achieved:
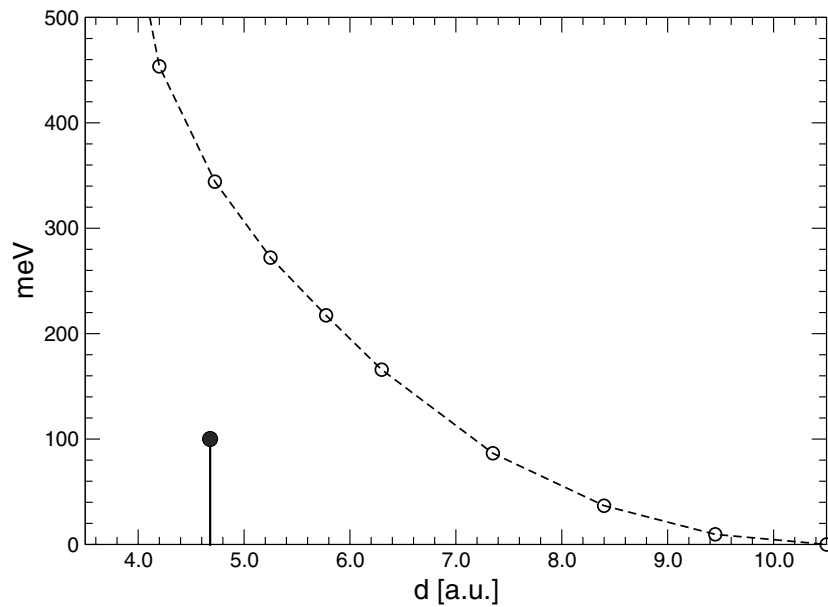
Figure 1. The total pair potential contribution $J_{\binom{2}{2}}^{(2)}$ to the expansion coefficient $J^{(2)}$ for NiAl calculated in the local density approximation [12] (open circles). The calculations were carried out in a box of 21 au length. No correction for interactions across the box was made and $J_{\binom{2}{2}}^{(2)}$ was set to zero at $d = 10.5$ au. Cluster expansion for NiAl on a fcc lattice gives a value of $J^{(2)} \approx 100$ meV (closed circle) in the nearest-neighbour shell. Thus many-body interactions screen the contributions of the pair potential to the pair expansion coefficient $J^{(2)}$ by roughly 70%.

- It is generally assumed but to the best of our knowledge nowhere rigorously proved so far that the adiabatic energy surface of a system of atoms can be evaluated in terms of a series of structure independent, perfectly transferable many-body potentials. We have given an explicit proof that this is indeed possible, and we have given a prescription for obtaining perfectly transferable many-body potentials by means of *ab initio* total energy calculations for isolated subclusters of the system.

- So far the cluster expansion method has mainly been applied to describe the ordering degrees of freedom in multicomponent lattice systems. We showed how the many-body potential expansion (cluster potentials), which often focuses on the positional degrees of freedom, can be merged with the cluster expansion method into a generalized cluster expansion which encompasses both ordering and positional degrees of freedom.

- Often the adiabatic energy hypersurface is parametrized by empirical cluster functionals [2]. We have demonstrated that mapping given cluster functionals into perfectly transferable many-body potentials can be used to compare different cluster functionals.

- We have shown how the coefficients of the cluster expansion method can be related to cluster functionals via the expansion of the cluster functional in transferable many-body potentials. Provided that, for example, accurate cluster functionals for a given system exist, the cluster expansion coefficients can then be constructed from local potentials.

Acknowledgment

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