



Analyzing the properties of clusters: Structural similarity and heat capacity



Yi Dong^{a,b,*}, Michael Springborg^{a,b}, Yong Pang^a, Francisco Morales Morillon^{a,c}

^aPhysical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, Germany

^bSchool of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China

^cFacultad de Ciencias, Universidad Nacional Autonoma de Mexico, 04510 Mexico, DF, Mexico

ARTICLE INFO

Article history:

Received 13 May 2013

Received in revised form 4 June 2013

Accepted 5 June 2013

Available online 2 July 2013

Keywords:

Similarity

Heat capacity

Silicon clusters

Germanium clusters

Silicon-germanium clusters

Vibrational properties

ABSTRACT

Two approaches for extracting information on clusters from unbiased structure-optimization calculations on a larger set of cluster sizes are presented. At first, we study how structural similarity can be quantified and present an approach that seems to match what subjectively would be expected. Second, we present a method for calculating the vibrational contributions to the heat capacities of the clusters. As test systems we have applied the methods to Si_n , Ge_n , and Si_nGe_n clusters with up to 44 atoms in total.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Theoretical studies devoted to the development of a general understanding of the relations between properties on the one hand and size and stoichiometries on the other hand of larger systems are obscured by several aspects. First of all, such studies require that the proper structures, i.e., those of the lowest total energy, are identified for a larger range of systems. However, for commonly used electronic-structure methods the computational costs for calculating the properties for just a single structure scale with the size of the system, measured in, e.g., the number of electrons of nuclei, to some power that typically is 3 or larger. Therefore, even for medium-sized systems these computational demands can put serious limits on what is possible. Independently of this scaling issue, another, complementary, problem leads to further complications. Thus, it has been shown that the number of nonequivalent minima on the total-energy surface grows faster than any polynomial in the size of the system [1]. These problems are well-known and several strategies have been proposed to meet those, see, e.g., [2–7].

There is, however, a third issue that has been given less attention. Such calculations as the ones mentioned above will provide,

* Corresponding author at: Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, Germany.

E-mail addresses: y.dong@mx.uni-saarland.de (Y. Dong), m.springborg@mx.uni-saarland.de (M. Springborg), pangdayong@hotmail.com (Y. Pang), pacomm@ciencias.unam.mx (F.M. Morillon).

at first, total energies as well as the coordinates of the various nuclei for a smaller or larger set of sizes and/or stoichiometries. In many cases, also other information like the spatial distributions and energies of the electronic orbitals is obtained. Thus, it is often far from trivial to reduce this large information to some few key quantities that describe the development of the properties of the systems with size and/or stoichiometry in a simple, although concise way that ultimately will allow for the development of a more general chemical or physical understanding.

In the present contribution we shall focus on this last issue and, thereby, use a set of clusters as the systems of our interest. During the last years we have developed various descriptors aimed at identifying general trends in structure and energetics of clusters (see, e.g., [6,7]), but, as we shall argue below, not all those are optimal and improvements as well as further descriptors may be (more) useful.

The systems we shall consider are Si_n , Ge_n , and Si_nGe_n clusters with up to a total of 44 atoms. For those, we have previously reported results of an unbiased structure optimization study [8]. In that study, we used a parametrized, density-functional, tight-binding method in calculating the total energy for a given structure in combination with a genetic-algorithm approach for an unbiased structure optimization. The purpose of the present study is not to discuss the properties of those clusters specifically, neither to address the accuracy of the computational approach. Rather, we shall

use those results as a pool that here is analyzed using the tools that we shall describe below.

Specifically, we shall in this contribution present results for a new approach for quantifying structural similarity between different clusters as well as present results of a recently developed approach for studying heat capacities for the clusters as a function of their size and the temperature. Since our approach is based on earlier works, we shall in the next section review some of those. Subsequently, we shall in Section 3 describe our theoretical approach and in Section 4 the results. Finally, our results are summarized in Section 5.

2. Previous work

2.1. Structural similarity

In earlier works [9,10] we have introduced descriptors, so called similarity functions, that were developed in order to quantify structural similarity. We shall here briefly outline their basic ideas, also because we will use these for comparison with the new measures and since we will discuss their limitations.

We consider two different systems, A and B, and want to study, whether the system A can be considered more or less similar to a part of system B. An example could be that A is an optimized structure of a cluster with N atoms, whereas B is a (larger) part of a crystal or is another cluster, having M atoms. We assume that $M \geq N$.

The structure of A is characterized by N positions, $\vec{R}_{A,i}$, $i = 1, 2, \dots, N$, whereas we for B have $\vec{R}_{B,i}$, $i = 1, 2, \dots, M$. It is useful to define the center for each system,

$$\begin{aligned}\vec{R}_{A,0} &= \frac{1}{N} \sum_{i=1}^N \vec{R}_{A,i} \\ \vec{R}_{B,0} &= \frac{1}{M} \sum_{i=1}^M \vec{R}_{B,i}.\end{aligned}\quad (1)$$

Subsequently, we define scaled positions relative to the centers,

$$\begin{aligned}\vec{r}_{A,i} &= (\vec{R}_{A,i} - \vec{R}_{A,0})/u_A, \quad i = 1, 2, \dots, N \\ \vec{r}_{B,i} &= (\vec{R}_{B,i} - \vec{R}_{B,0})/u_B, \quad i = 1, 2, \dots, M.\end{aligned}\quad (2)$$

u_A and u_B are pre-chosen, fixed scaling parameters that may be different for the two systems.

If $M = N$ we may use the two sets of interatomic distances

$$\begin{aligned}d_{A,ij} &= |\vec{r}_{A,i} - \vec{r}_{A,j}| \\ d_{B,ij} &= |\vec{r}_{B,i} - \vec{r}_{B,j}|,\end{aligned}\quad (3)$$

that we will sort in increasing order, in order to quantify the structural similarity. I.e., we will consider

$$\begin{aligned}Q &= \frac{1}{K} \sum_{i=1}^K (s_{A,i} - s_{B,i})^2 \\ S &= \frac{1}{1 + Q^{1/2}}.\end{aligned}\quad (4)$$

Here, $K = \frac{M(M-1)}{2}$ is the number of terms in the summation. Finally, $s_{A,i}$ and $s_{B,i}$ are either the sorted, scaled, interatomic distances, or the sorted, scaled, inverse, interatomic distances. In the former case, Q may have dominating contributions from atoms that are far apart, whereas similarity among close neighbors is given less importance. In order to try to give more emphasis on the near surroundings of the individual atoms, we have, therefore, also considered the case that Q is calculated from the inverse interatomic distances.

For $M = N$ not very small, K is much larger than the number of coordinates, $3M = 3N$, that is needed to specify the structure

uniquely. Thus, in that case the approach should be able to quantify structural similarity. However, for $M > N$ difficulties show up.

The simplest case is that of $M = N + 1$, which happens when, e.g., trying to quantify growth patterns, i.e., to quantify whether the cluster with $N + 1$ atoms is similar to the one with N atoms plus an extra atom. In that case, we modified the approach slightly by considering all those $M = N + 1$ structures that could be generated from the cluster with $M = N + 1$ atoms by removing a single atom and keeping the positions of the remaining N atoms unchanged. For each of those $M = N + 1$ structures with N atoms we calculated a similarity function from Eq. (4) and ultimately chosen the largest value of those.

Also for $M = N + 2$ a similar approach can be applied. Then, we will consider all the $\frac{M(M-1)}{2}$ structures that can be constructed from the cluster with $M = N + 2$ atoms by removing two atoms and keeping the positions of the remaining atoms fixed. As above, we calculate a similarity function from Eq. (4) and ultimately chose the largest value of those $\frac{M(M-1)}{2}$ different ones.

But if M and N differ by much more than 1 this approach becomes increasingly prohibitive, and in the extreme case that $M \rightarrow \infty$, which, e.g., is the case when comparing the cluster with N atoms with the crystalline material, the approach above cannot be used.

As a simplification we, therefore, suggested to base the similarity function on the scaled radial distances,

$$\begin{aligned}r_{A,i} &= |\vec{r}_{A,i}| \\ r_{B,i} &= |\vec{r}_{B,i}|.\end{aligned}\quad (5)$$

Also these are sorted and S is defined as in Eq. (4). Then, $K = N$, and $s_{A,i}$ and $s_{B,i}$ are either the sorted radial distances or the sorted, inverse, radial distances. Then, the two cases distinguish between whether the outermost or the innermost atoms are given most importance.

This approach works reasonably well as long as the two structures that are to be compared both are compact. This was the case for most of the systems we have looked at so far, but if the structures are less compact problems may easily show up. Thus, when comparing a hollow nanoparticle (for instance, a C_{60} molecule) with one that is filled with some atoms, the approach would find that the two structures are markedly different, although intuition would tell that they share many features, i.e., the shell. Moreover, if the larger system is, again, the crystal for which $M \rightarrow \infty$, there is an ambiguity in the definition of the center [cf. Eq. (1)] making the similarity function non-unique. Furthermore, in that case, the radial distances would not be able to identify the structural similarity between an elongated cut-out of the crystal and the crystal itself. On the other hand, S may predict close structural similarity in cases where intuition would say the opposite. Thus, a square and a tetrahedron may be found to be identical (by proper choice of the lengths of the sides).

Other approaches that have been devised to quantify structural similarity are mainly used for comparing structures of the same size. This is important in the structure-optimization procedure since it can be used to avoid that similar structures are been treated more than one time. This is, e.g., the case for the approach by Lee et al. [11]. Using two different cut-off distances, $d_1 < d_2$, they calculated for each atom the number of atoms, n_1 , within d_1 from the reference atom and the number of atoms, n_2 , with a distance between d_1 and d_2 of the reference atom. Thereby, they get for each of the two structures to be compared two sets of numbers $H_1(n)$ and $H_2(n)$, respectively, which give the number of atoms with $n_1 = n$ and $n_2 = n$, respectively. Finally, the differences between $H_1(n)$ and $H_2(n)$ is used in identifying structural similarity. In a typical, closed-packed system, n can at most be of the order of 10, meaning that the structural information is reduced to roughly 20

Download English Version:

<https://daneshyari.com/en/article/5393916>

Download Persian Version:

<https://daneshyari.com/article/5393916>

[Daneshyari.com](https://daneshyari.com)