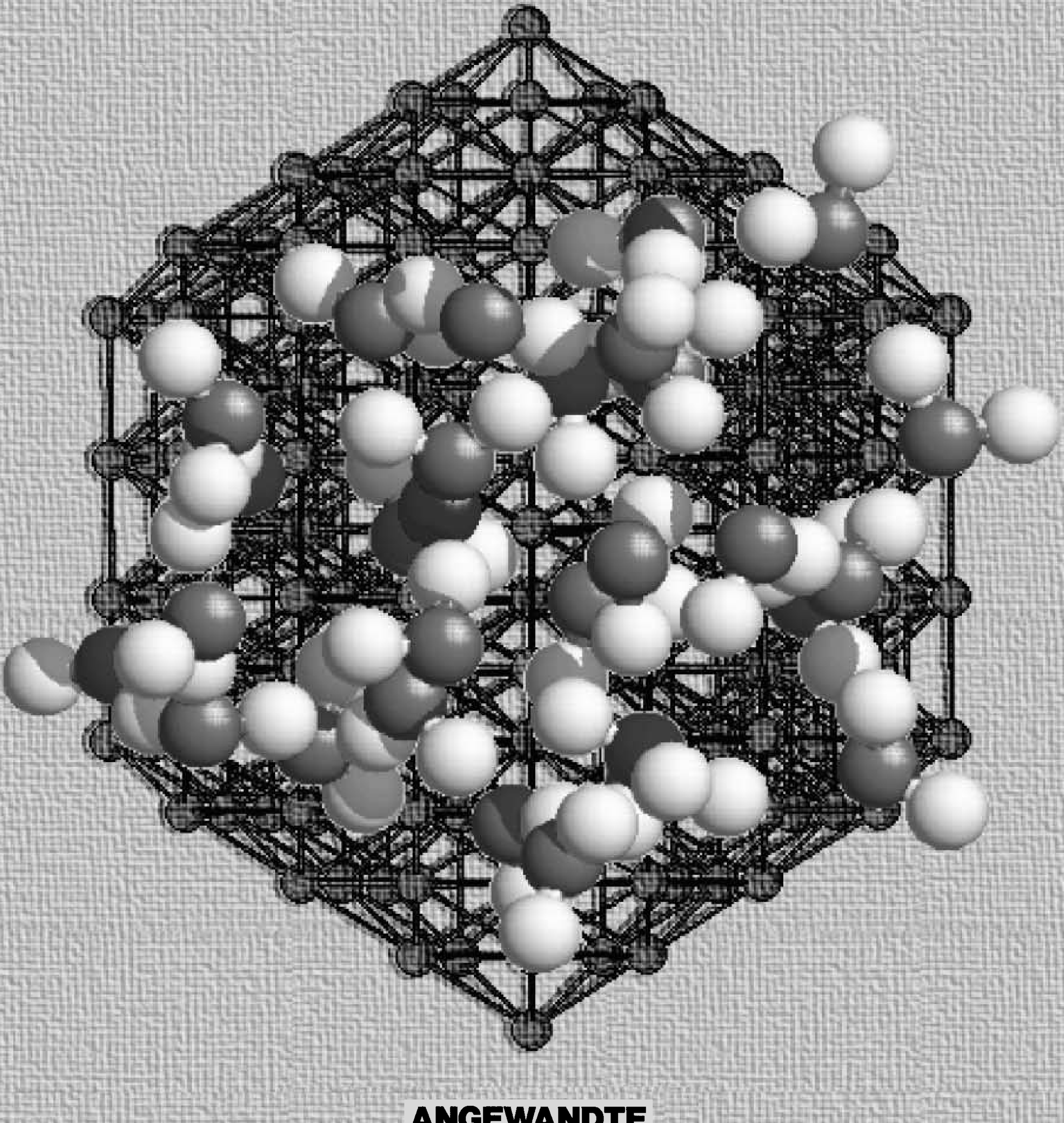
What do noble-gas clusters (background) and
apparently amorphous water clusters
(foreground) have in common?
Their structures change with cluster size.



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Structural Transitions in Clusters[**]

Bernd Hartke[*]

If one adds more particles to a cluster, the energetically optimal structure is neither preserved nor does it change in a continuous fashion. Instead, one finds several cluster size regions where one structural principle dominates almost without exception, and rather narrow boundary regions in-between. The structure of the solid is usually reached only at relatively large sizes, after more than one structural transition. The occurrence of this general phenomenon of size-dependent structural transitions does not seem to depend on the nature of the particles, it is found for atomic, molecular, homogeneous, and heterogeneous clusters alike. Clearly, it is a collective many-body phenomenon which can in principle be calculated but not understood in a fully reductionistic manner. Actual calculations with sufficient accuracy are not feasible today, because of the enormous computational expense, even when unconventional evolutionary algorithms are employed for global geometry optimization. Therefore, simple rules for cluster structures are highly desirable. In fact, we are dealing here not just with the academic quest for linkages between cluster structure and features of the potential energy surface, but structural transitions in clusters are also of immediate relevance for many natural and industrial processes, ranging from crystal growth all the way to nanotechnology. This article provides an exemplary overview of research on this topic, from simple model systems where first qualitative explanations start to be successful, up to more realistic complex systems which are still beyond our understanding.

Keywords: aggregation · cluster compounds · global optimization · magic numbers · structure elucidation

1. Introduction

1.1. Importance of Clusters

In the present article, we are not interested in the clusters of inorganic or organometallic chemistry,[1, 2] with comparatively few (transition) (metal) atoms next to each other, surrounded by numerous ligands and (possibly complicated) counterions, needed to make the formation and stability of these clusters possible. We are also not interested in ligand-covered nanoparticles,[3, 4] now generated and examined in many experiments and by some theoreticians. Instead, our focus is on "naked" clusters, with, as experimental reference, the molecular beams used by physical chemists or molecular physicists.

Nevertheless, these clusters are by no means elusive curiosities of the laboratory. They are of prime importance in many industrial and natural processes, for example in chemical vapor deposition (CVD)[6] or in all variants of nanotechnology,[7–10] but also in the wide area of aerosols. There, many current studies investigate mixed clusters of ice and sulfuric acid, and their role in ozone depletion in polar stratospheric clouds.[11]

From the viewpoint of basic theoretical research, clusters form the link between the thoroughly investigated and hence largely well understood world of single molecules and the world of the "infinitely extended" condensed phase, which is also quite accessible with the special methods of this area. This basic interest in clusters culminates in several fundamental questions, for example: at which minimum size does a cluster start to exhibit metallic properties?[12, 13] In Section 1.2, we argue that even this primary issue of cluster structure is still largely unresolved.

While theoretical treatments of single molecules and also of the periodic solid state are almost routine today, the intermediate region of clusters still constitutes a challenge, for several reasons: These clusters are definitely too large for ab initio calculations, including sophisticated treatments of electron correlation, but empirical potentials often are not sufficiently accurate. The scaling of computational expense with system size still is a problem, in spite of the latest developments in linear scaling ab initio theories;[14] even the more elaborated empirical potentials can be too expensive for large clusters. And even without using modern catchwords

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[**] The abbreviations used in this article are listed in Table 1.

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such as complexity and emergent phenomena, we will conclude in Section 2.2 that investigations of clusters need new theoretical principles and techniques.

1.2. Structure of Clusters

The reason that clusters are called clusters and are not simply called molecules is mainly because we do not yet know any simple rules for their structure. The historical hypothesis that clusters are simply pieces of the corresponding solid was disproved very early on.[15]

Today the opposite proposition is commonly accepted: in general, the structure of small clusters is quite different from that of the "infinitely extended" solid, often even with (local) symmetry elements not allowed in periodic crystals, such as fivefold rotation axes. Unfortunately, this is a negative statement, not leading to any construction principle for clusters. However, a simple argument in favor of this updated proposition does contain at least one possible construction scheme.

It is tempting to ascribe the structural differences between clusters and the solid state to the dominance of surface effects, but this is rather vague and unconstructive; in fact, attempts in this direction can even be misleading, for example in attempts to understand the structures of silicon clusters.[16, 17] Instead, we want to recall an argument that has been present in the literature for a long time (see Nelson and Spaepen[18] and the historical references listed there): Imagine a species of atoms interacting like hard spheres or by a somewhat more realistic pair potential (such as the Lennard–Jones (LJ) potential, see Section 3.1; all the abbreviations used are given in Table 1). Arranging these atoms in three dimensions, one can retain optimal packing up to a tetrahedron of four atoms, by maximizing the number of direct contacts or of the number of atom pairs at optimal pair distance. Adding more atoms, it seems to be possible to remain in this state of optimal packing, by generating further tetrahedra. While something like this is actually possible in two dimensions, three-dimensional space cannot be filled with tetrahedra. As shown in Figure 1, suitable arrangements of tetrahedra lead almost to a pentagonal bipyramid and then almost to an icosahedron—but not exactly. According to the preferred terminology, there remains a gap, the system is "frustrated", or it becomes impossible to have all nearest neighbors at the optimal pair distance. Figure 1 also depicts the two possibilities of arranging the deviations from optimal pair distances, either in one place, or by distributing them evenly across the cluster. As mentioned below in Section 3.1, these deviations lead to the concept of "strain" in a cluster and to a first qualitative explanation for some structural transitions.

Table 1. Summary of the abbreviations in this article and the section in which they are first used.

Abbreviation	Definition	Section
CCSD(T)	coupled cluster (method including all) single and double (excitations including the) triple (excitations from perturbation theory)	3.4
CPMD	Car–Parrinello MD	2.1
DC	differential convex	2.2.2
DFT	density functional theory	2.1
EA	evolutionary algorithm	2.2.2
fcc	face-centered cubic	3.1
GA	genetic algorithm	2.2.2
GVB	general valence bond theory	2.2.3
hcp	hexagonal close packed	3.1
HF	Hartree–Fock	3.5
LJ	Lennard–Jones	1.2
MC	Monte Carlo	2.1
MD	molecular dynamics	2.1
(L)MP2	(Local) Møller–Plesset perturbation theory 2nd order	3.5
NP	nondeterminist polynomial	2.2.2
OPLS	Optimized potentials for liquid simulations	3.6
QCISD	quadratic configuration interaction (limited to) single (and) double (excitations)	3.3
QMC	quantum Monte Carlo	3.5
rcp	random close packed	3.1
SA	simulated annealing	2.2.2
SCF	self consistent field	2.2.3
TB	tight binding	3.3
TIP4P	transferable intermolecular potential with 4 points	3.5
TTM2-F(R)	Thole-type model 2, flexible (rigid)	3.5
TTP	tetracapped trigonal prism	3.3

Bernd Hartke, born 1963 in Concepción (Chile), studied chemistry at the University of Würzburg (Germany). After his diploma in 1988, he obtained his Ph.D. in 1990 with a thesis on quantum-mechanical wavepacket dynamics under the supervision of Professor Jörn Manz. For the following two years, he worked on implementations of direct ab initio molecular dynamics as a Liebig fellow of the Fonds der Chemischen Industrie with Professor Emily Carter at the University of California, Los Angeles. In 1992, he started working towards his Habilitation in the group of Professor Hans-Joachim Werner, first at the University of Bielefeld and, since 1994, at the University of Stuttgart. During this time, he broadened his research interests towards global geometry optimization of clusters using evolutionary algorithms. He obtained his Habilitation in theoretical chemistry in 1998, with a thesis that also covered time-independent quantum-mechanical reactive scattering. In 2000, he was awarded a Karl-Winnacker scholarship. In 2001, he accepted a position of full professor for theoretical chemistry at the University of Kiel.

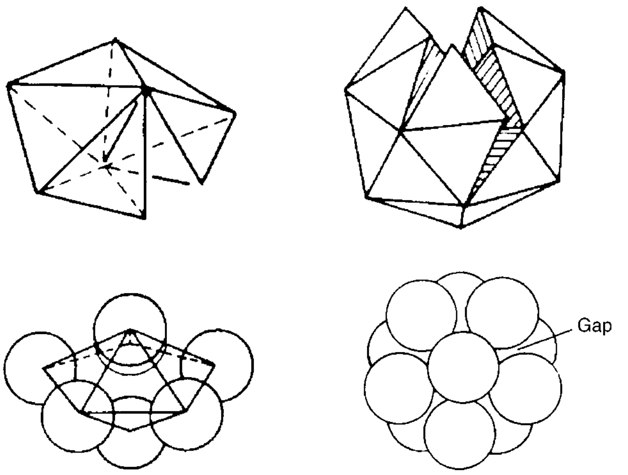


Figure 1. Suitable packing of tetrahedrons in three dimensions almost leads to a pentagonal bipyramid (left column) and to an icosahedron (right column); reproduced with permission from ref. [18].

Restricting ourselves for the moment to particles interacting through such simple pair forces, this line of thought proposes geometries with fivefold rotation axes (the icosahedral structural principle) as a quasi-natural structural scheme for small clusters. In the periodic crystal, however, symmetries of this kind are not allowed. Therefore, even without the problem of frustration, it is not possible to continue packing tetrahedra all the way to the periodic solid state. Hence, upon the successive enlargement of a cluster, there has to be at least one or even several transitions that change of the basic structural principle. (Local polytetrahedral order is indeed possible in extended nonperiodic systems, as in glasses or quasicrystals, which leads to interesting phenomena;[18] but this is not the main topic of this article.)

If the forces between the particles in the cluster are more complicated, and at least as important as the simple sterical packing argument, further and different basic structures have to be expected for small clusters. However, it should have become clear by now that also in these cases we are likely to see differences between cluster and crystal structures.

Martin et al.[19, 20] has given a detailed description and analysis of several generic possibilities for packing, together with simple equations relating the number of particles and the number of geometrical shells in the cluster. These ideas can be used to predict and interpret prominent magic numbers as shell closures in these different structural principles, and is important for the interpretation of experiments, but in itself it does not explain the preference of certain packing modes at certain cluster sizes. Searching for explanations for the size dependence of cluster structures and properties, beyond this simple steric packing argument, one frequently meets two models:

1) Physicists like to use the "jellium" model.[21] When electronic effects dominate, for example, in clusters of alkali metals, it can explain several magic numbers. There is, however, no cluster structure (of ionic cores or atoms) in this model, but only a diffuse, positively charged background or a largely empirical external potential for the electrons. With these assumptions, it is hard to apply this model to the present problem, where a detailed description of the inner cluster structure is called for, while the outer form remains qualitatively the same.
2) The "liquid-drop" model was developed for extrapolation from larger to smaller clusters. Jortner[22] gives historical references and explains the model, which is again founded on a simple geometry argument. This model succeeds in reproduction and prediction of smooth trends in large clusters, and provides the basis for the usual plots of properties versus $n^{-1/3}$ (where n is the number of particles in the cluster). It has become common to diagnose magic numbers and transitions as deviations from linearity in such plots. In the last 15 years several authors[23–25] extended the model with corner and edge contributions, but it still does not take the inner structure of clusters into account. Therefore, it has to fail for the construction of small clusters, where inner structure is important, as was pointed out in the original articles.[22]

Therefore, as soon as the inner structure of clusters becomes unimportant (because of electronic effects or simply because of cluster size), we are able to interpret and understand (smooth) changes in their properties. But for the interesting region of smaller and nonmetallic clusters (comprising small clusters of metal atoms, and small clusters are always nonmetallic even when they contain metal atoms), which are dominated by the inner structure, basic understanding is still lacking.

According to the simple packing argument (see above), it seems to be clear that there have to be size-dependent structural transitions in clusters, at least for certain classes of potentials (or if certain types of interactions between particles in the cluster dominate). Without expensive calculations (cf. examples in Section 3), nobody can predict the cluster sizes where these transitions occur. That is, we still do not have qualitative and easily understandable connections between the potential energy surface and these transitions; they still have the status of typical "emergent phenomena" of many-particle systems.

It is also still largely unknown how such a transition actually occurs, with the successive addition of particles. It is hard to imagine a gradual transition from one structural principle to a new one, since it can be expected that mixed or partially disordered structures have much higher energies (see, however, ref. [26] for a model comprising several structures). And it is equally hard to imagine a sudden change of the whole cluster structure upon addition of just one more particle. In fact, at sufficiently low temperatures only those clusters can grow into the "correctly" ordered bulk phase that already start their growth within this structure. In this scenario, successful seeds in the collection of small clusters have only locally minimal energy, whereas the globally minimal energy structures turn out to be dead ends for crystal growth. More detailed understanding can only arise from dynamical simulations with atomic resolution at various temperatures, but work of this type is still rare.

In the area of these size-dependent structural transitions of clusters, this article gives an overview of the current state of the art and accentuates the central problems that still need to be solved. It should be emphasized that this problem area is not just of academic interest. All the questions mentioned above have direct relevance for phenomena such as, crystallization, seed formation and growth, or solid–liquid phase transitions in extended systems.[27, 28]

These structural transitions should also be compared and contrasted with solid–liquid phase transitions in clusters: the latter occur as a function of temperature, the former as a function of the number of particles. However, transitions between structures that occur with changes in the number of particles have also already been theoretically predicted to occur with temperature changes.[29] Recently, there has been a surge of interest in temperature-dependent transitions, because now there are not only theoretical studies of phase transitions and coexistence in clusters[30–33] but also direct experimental observations.[34] Nevertheless, solid–liquid phase transitions in clusters are not the main topic here.

Similarly, there are analogies and differences between the general problem of cluster structure and the abstract three-dimensional geometrical packing problem: Typical packing problems are formulated with rigid, (periodically) repeated units, and hence are more directly comparable with crystal-structure prediction. In fact, there are now the first connections between abstract geometrical tiling and crystallography.[35–37] In clusters, however, we are dealing with (to some degree) nonrigid units and with surface effects (or different boundary conditions).

Section 2 briefly introduces and compares several traditional and new theoretical methods for investigating cluster structures, with global geometry optimization by evolutionary algorithms treated in more detail. In Section 3, examples for characteristic structural transitions in various cluster systems are given, with some bias towards the work of our group. The main findings are then summarized in the final Section 4.

2. Theoretical Methods

2.1. Traditional Techniques

To save space, we do not give a comprehensive introduction nor an overview of applications for these techniques. Only the suitability of several methods for our present problem will be discussed.

Molecular dynamics (MD)[38, 39] and Monte Carlo (MC)[38, 39] with empirical potentials are long established methods to deal with structure and dynamics of molecules. In recent years, these have been joined by variants that do not need a prefabricated potential energy surface, since this information is generated during the calculation at each current configuration. The most popular one of these is Car–Parrinello MD (CPMD),[40, 41] where the atoms follow classical trajectories and the forces between them are calculated with density functional theory (DFT) methods. Decisive savings in computer time arise from substituting the costly solution of the quantum chemical eigenvalue problem in a huge basis of plane waves by fictitious dynamics of the wavefunction coefficients, which dynamically adjusts the wavefunction to the movements of the nuclei. Extensions of this method are direct DFT versions[42] of the path-integral technique[43, 44] and direct-DFT versions[45] of the so-called "centroid MD",[46] which allows a quantum mechanical treatment of the nuclear dynamics. Extensions in another direction, going beyond DFT to a full ab initio treatment of the electronic problem, have also been implemented several times.[47–49] An excellent and detailed comparison of these methods was recently published by Dominik Marx and Jürg Hutter.[50]

Applied to the problem of interest here, all these methods offer some advantages, at least in principle. They give direct access to thermodynamic quantities and suitably averaged structural information at experimentally relevant temperatures.[51] As long as actual molecular dynamics are performed, they also offer direct insight into dynamical processes, in the case of classical MD on empirical potentials even for very large biochemical systems.[52, 53] But there are also some disadvantages. Path integrals only give (quantum) statistical mean values, no true quantum dynamics of the nuclei ("centroid MD" does provide semiclassical dynamic of the nuclei). For large systems, one cannot even approximate quantum dynamics with purely classical dynamics (in the sense of a quasiclassical treatment, as in typical reaction dynamics applications). For these reasons, the explicit insight into dynamics is actually limited to more or less representative single trajectories.

For sufficiently good statistics and systems of nontrivial size, the computational expense is very large, even for classical dynamics on empirical potentials. Substituting empirical potentials with direct DFT or ab initio treatments puts severe limitations on the treatable statistics and/or system size, even today. As a representative example, we mention the CPMD calculation performed by Chelikowsky and Dean on the thermodynamic quantities for Si_n,[51] which had to stop at $n = 5$ in spite of the use of supercomputers. A treatment at the DFT level may not be good enough for certain systems, and with the more reliable treatment of electron correlation in ab initio methods any approach to larger systems becomes completely impossible.

2.2. Alternative and Complementary Approach: Global Geometry Optimization

Considering the difficulties of methods aiming at complete dynamics or statistics, alternatives appear desirable. A simple hypothesis states that the cluster structure most likely to be found in experiments corresponds to the minimum of lowest energy on the potential energy surface (the justification of this hypothesis is discussed in Section 2.2.3). Therefore, alternative methods are those that are able to locate the global minimum among a large set of local minima, that is, global optimization methods.

2.2.1. Importance of Global Optimization in Chemistry

Actually, many-body problems are prevalent everywhere in chemistry. All systems under study consist of many electrons, many atoms, and perhaps even many molecules. Hence, one could expect to see global optimization being used very often. There are several reasons why this is not the case:

1. In the electronic configuration (with the nuclei kept fixed) present-day knowledge indicates that multiple minima are not problematic and rare, at least in the vicinity of equilibrium structures. Accordingly, this aspect of the electronic problem is not discussed and with few exceptions not even mentioned in most textbooks.[54]
2. On the other side of the Born–Oppenheimer separation we face the problem of the nuclei. Here, extensive prior knowledge about chemical structures and reactions leads to accurate guesses for structures of traditional molecules, which then only need to be optimized locally. For this reason, efficient local-optimization routines are present in every (quantum) chemical program package, while global ones are usually lacking. This approach does not work anymore for supramolecular structures, clusters, and similar systems; but this was not a pressing concern since structures of this size were not amenable to exact calculations anyway, until recently.

Nevertheless, various global optimization methods are currently being used in many areas of chemistry, a few examples are: the actual control of chemical reactions with lasers (following the basic idea "teaching lasers to control molecules" of Judson and Rabitz;[55] this approach was realized experimentally in 1998[56]), "molecular docking" in pharmaceutical lead discovery,[57, 58] analysis and prediction of protein folding,[58, 59] crystal-structure analysis[58, 60] and prediction.[61, 62] A review by Judson[63] gives several other applications, with a focus on evolutionary algorithms.

2.2.2. Global Optimization Methods

In contrast to a common prejudice, local and global optimization are two very different tasks, requiring very different solution strategies. In local optimization, we have a general, problem-independent model (approximation by a quadratic form), which substantially enhances the efficiency of many methods; currently, such a model is unknown in global optimization. In local optimization, further information on the function to be optimized, in the form of first and second derivatives, is very useful; the local character of this information makes it largely useless in global optimization. Local optimization depends on the starting point by definition; whereas global optimization is independent of it, in fact, this is an important criterion for its success. Local optimization has a natural, universal end which is easy to test; whereas there is no safe termination criterion in practically relevant global optimization.

Another important difference in practice is the scaling of computational effort with problem size. Modern local algorithms scale only quadratically.[64, 65] General global methods (without prior information on the structure of the function to be optimized) that actually give a guarantee for finding the global optimum scale exponentially, at least in the present application: It was demonstrated in an abstract fashion (independent of any potential) that global cluster geometry optimization is an NP-hard problem (Table 1).[66–69] This result means in practice that the search space and with it also the number of local minima increases exponentially, as was empirically found for small LJ clusters a long time ago.[67, 70] Apparently, this is not only a basic problem for global optimization but also one of the reasons for intrinsic difficulties of any MD simulation of larger systems.

Such exact, deterministic methods (with a guarantee for finding the global optimum) exist in many variants today and are treated in standard monographs.[71, 72] We will not further address these methods here, since their applications are limited to small systems, because of the NP character of the problem and to the implicit need for searching the complete configuration space. In the standard benchmark system of Lennard-Jones clusters (cf. Section 3.1), a DC transformation (Table 1) could be applied in exact form only up to $n=7$;[73] a homotopy method could handle clusters up to $n=31$ (which are still trivially small for the methods discussed below) but surprisingly failed for three smaller cases.[74]

This is the basis for practical relevance of "nonexact, nondeterministic" methods. There, the guarantee for finding the global optimum is deliberately dropped, in favor of a higher efficiency, which makes it possible to treat much larger systems. In the following, "global optimization" always means one of these nonexact methods. Because of the limited space available, we will not give an overview over all these methods, but only a brief, exemplary discussion of a few prominent algorithms.

The factual standard procedure in theoretical chemistry consists of successive local optimizations with excessive use of external prior information. The choice of initial starting points for local optimizations can be automated in several ways:[72] simple random search, systematic grid search, "branch and bound" approaches, or selection of points on classical trajectories. Alternatively or additionally, arbitrary amounts of prior information can enter the choice of initial points. In any case, for a growing number of initial points the method converges towards a quasideterministic algorithm with an effective guarantee for finding the global optimum, simply because at some stage all the minima will have been found. But this is a rather theoretical limit; already for medium-sized clusters, this method will generally fail in practice, because of the exponential size scaling of the search space. The chances of missing whole regions of configuration space are already dangerously high for applications to small clusters. As an example, we mention the discovery of a clearly physically wrong global minima on a very elaborate silicon potential by using evolutionary algorithms,[75] which escaped the attention of the authors of this potential[76] when using successive local optimizations, in spite of their otherwise very careful work.

After its introduction,[77] "simulated annealing" (SA) quickly became fashionable as a quasigeneral global optimization tool; but nowadays it faces some criticism: Computational expense is rather high compared to the final result (ideally just the global optimum), information permanently generated during the algorithm is not really used later, and finding the optimal cooling schedule turns out to be problematic in practice. There is a deplorable lack of fair comparisons, but from my experience, SA in its original forms is not competitive with evolutionary algorithms for global cluster geometry optimization.

Recently, a distant relative of SA has gained interest, the so-called "basin hopping". This method was introduced by Li and Scheraga[78] for protein folding and adapted by Wales and Doye[79] to the problem of cluster structure; meanwhile, there are also applications in other areas.[80] Basically, this algorithm does a series of MC steps, which are followed by local minimizations; this corresponds to an MC treatment on a modified potential energy surface, which is transformed by the local minimizations to a series of plateaus and steps with fewer and lower barriers in-between; this is diagnosed as the basis of the success for this method. Because of the large number of local minimizations, computational expense is rather high for this method. Nevertheless, it seems to be the most efficient method today for small LJ clusters[79] up to about $n = 100$. Its size scaling is approximately n^5, though, which limits its applicability to larger systems.

In the methods mentioned so far, one typically finds iterative improvement of single points in configuration space (that is, of cluster structures) without any exchange of information. In contrast, evolutionary algorithms (EA) are based on different ideas: A whole "population" of different cluster structures is treated quasi-simultaneously (which makes an efficient coarse-grained parallelization very easy). Various operators, some of them modeled after natural evolution, change these structures ("mutation") or exchange (partial) structural information between them ("crossover"). This generates from the initial (random) population a new "generation" of cluster structures. Iterating this scheme over many generations results in a global optimization algorithm, and again a general one. Its result is not only the global optimum (upon convergence), but also a list of several good local optima. EAs are not new; the basic idea surfaced in the 1950s and was then rediscovered independently at least ten times (Fogel[81] gives a historical account), sometimes under different names, for example genetic algorithms (GA), but these technical distinctions are largely obsolete today. A good introduction for beginners is given by Michalewicz and Fogel,[82] applications in chemistry have been collected by Judson[63] and applications to clusters by Johnston and Roberts,[83] see also the documentation of the most recent developments in ref. [84]. My pioneering work in applications of EAs to global cluster geometry optimization is given in ref. [85]. With important additions of other groups,[86, 87] these first steps could be developed into an efficient method,[88] as reliable and about as efficient as "basin hopping" for small LJ clusters, but because of its cubic size scaling applicable also to larger clusters (up to $n = 150$ already in ref. [88], and up to $n = 250$ in ref. [89]).

Systematic and fair comparisons of such methods are very rare in the literature, and often limited to small systems.[90] At least for the benchmark system of LJ clusters, which was treated with a wide variety of global optimization algorithms,[67] "basin hopping",[79] and EAs[88, 89] seem to be the only methods able to treat also the notoriously difficult cases $n = 75-77$ and $n = 102-104$ without prior information.

2.2.3. Status of the Global Optimization in Comparison to Traditional Approaches

For determinations of minimum energy structures, the expense of these alternative methods is smaller than for full MD calculations, because there is no need to generate statistically relevant trajectories. As results one gets directly the global minimum energy structure and energetically low-lying local minima. In comparison to typical MD and MC calculations, this allows a faster and more direct deduction of dependencies between terms in the potential energy function and structural preferences; this obviously simplifies the construction and improvement of empirical potentials for clusters. As for MD and MC, direct combinations of SA and EA methods with DFT calculations in simple or reduced form is possible for small systems and was already started several years ago.[91–94] Direct combinations of all of these methods with better ab initio calculations are not practicable in general, since the computational effort is extremely large. As an example, we could show that MD–SA on the generalized valence bond (GVB) level with a "large core" pseudopotential works as expected for Ni_5—in the sense that two trajectories starting from two totally different structures reached the same final minimum.[95] This level of treating the electronic structure, however, is not sufficient in this case: The planar W-structure we found turns out to be incorrect at higher levels. The correct structure presumably is that of a deformed trigonal bipyramid,[96a] experimental results[96b] seem to confirm this.

We tried an indirect approach and found this to be more successful: In an SCF-like cycle, global geometry optimizations on an empirical potential alternate with successively better fits of this empirical potential to ab initio single-point calculations (at just these minimum structures), by global optimization of the parameters in the empirical potential. Shortly after its introduction,[75] this strategy was applied successfully to atomic silicon clusters[97] and mercury clusters[98] as well as to molecular water clusters.[99] In practice, this method reliably yields the global minimum energy structures on the DFT or ab initio potential, and also an improved empirical potential.

As opposed to MD and MC calculations, global minimizations are purely static, in the sense of producing only the (classical) global minima of energy (enthalpy). With appropriate vibrational analyses of the sets of local minima, however, which are additionally obtained, one can extend the results up to full thermodynamic data,[100, 101] and with sufficiently large data sets of minima and transition-state geometries, through a master equation, approach even approximate relaxation dynamics.[102, 103] In spite of these possible refinements, MD and MC methods do not become superfluous; in my opinion these methods are complementary. For certain research aims, for example, the structural transitions envisaged here, or the relationship between potential and cluster structure, searching for the global minimum is an answer to the zeroth-order question. Effects of zero-point energy, finite temperatures, and cluster dynamics are secondary considerations. For many of the systems mentioned in Section 3, experiments do indeed find the global minimum energy structures. There are also counter examples, though, as demonstrated with the water hexamer (see Section 3.5). The identification of such cases as counter examples can still be done with global optimization, but further investigations have to include the traditional methods.

3. Exemplary Systems

3.1. LJ Clusters as Models for Noble-Gas Clusters

Clusters of noble-gas atoms are typically modeled using the LJ pair interaction. Stone's book[104] provides an introduction to this potential, including its partly absent physical basis, and shows improved alternatives.[105, 106] Hence, the LJ potential is mainly of historical importance, because of its analytical simplicity. But for this same reason it is still used in many places even today, for example, also as a compulsory benchmark system for global cluster geometry optimization methods. Extensive lists of structures and energies of global and local minima are available on the internet.[107, 108] There is such a vast amount of literature on this topic that perhaps every global optimization method in existence has at sometime been tested on this LJ benchmark system.[67, 70, 79, 87–89, 109] (Applications of this type to the more advanced noble-gas potentials are extremely rare.)

Therefore considering the huge amount of data known, the discovery of a new (fourth) structural type of LJ clusters in 1999, as a new global minimum for LJ_{98}, was quite a surprise.[110] This simple fact illustrates that the LJ system is all but simple, in spite of its simple potential functional form.

Figure 2 shows the four known basic structural types of LJ clusters, which feature different fundamental arrangements: Icosahedral structures are the logical continuation of the icosahedral scheme already introduced in Section 1.2, starting from the pentagonal bipyramid and continuing beyond the icosahedron itself by addition of further atom layers (which can happen in different ways.[108, 109]) The fcc (face-centered cubic) structures are sections from the fcc crystal. Decahedral structures can be visualized as an icosahedral core surrounded by fcc stacks. The new tetrahedral structures actually have a tetrahedron of atoms as the innermost core.

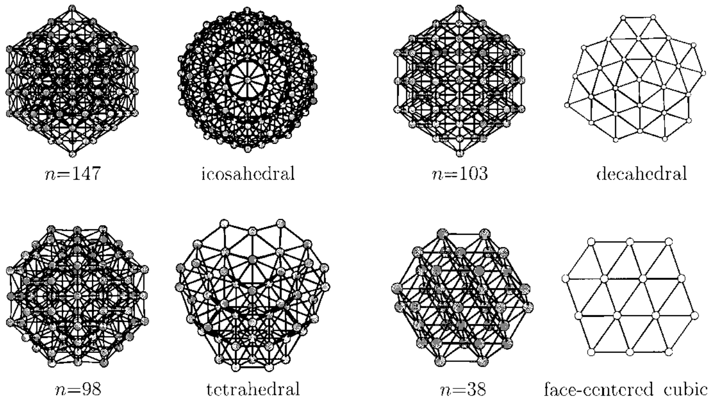


Figure 2. Pairs of views of each of the four basic structural types of LJ clusters; for each type: left: a projection that emphasizes the approximately spherical outer form; right: the same cluster in a different projection that emphasizes typical features of the inner structure (here, various numbers of atoms are projected on top of each other). At the number of atoms n indicated (but also at other cluster sizes), these structures have globally minimal energy; see text.

As mentioned in Section 1.2, icosahedral structures can be expected to be optimal, since they are (almost) a packing of tetrahedra and thus maximize the number of nearest neighbors. In three dimensions, however, such a packing cannot fill space exactly. Therefore deviations from the ideal pair distance arise, which can be interpreted as strain.[111, 112] This strain increases with cluster size. The other structural types are less strained, but have reduced numbers of nearest neighbors. Hence it comes as no surprise that the global minimum energy structures of smaller LJ clusters follow the icosahedral scheme almost without exception. this trend was analyzed in detail by Doye, Miller, and Wales, up to a size of $n = 80$[113] (Figure 3; at that time, the fourth tetrahedral structural type was still unknown): These and other investigations showed that fcc and decahedral structures come close in energy to the icosahedral ones only around cluster sizes $n = 38$, $n = 75-77$ and $n = 102-104$ and actually provide the global minima only at these particular cluster sizes themselves. These sizes are between the icosahedral shell closures of $n = 13,55,149,..$, but not exactly in the middle; in fact, there is no simple explanation yet for their occurrence at exactly these sizes. But even at these LJ cluster sizes, the search space is dominated by icosahedral structures, which makes these clusters particularly hard test cases for global optimization methods.

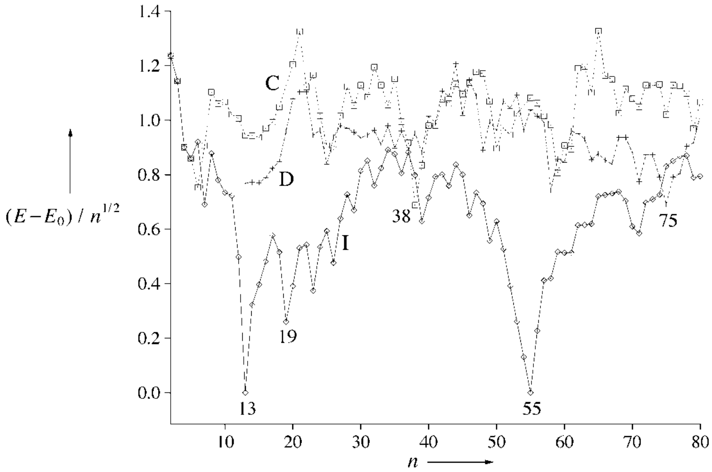


Figure 3. Competition between three of the four structural types of LJ clusters, in the size region up to $n = 80$: I = icosahedron, D = decahedron, C = face-centered cubic. The energy axis is scaled such that icosahedral clusters with closed shells ($n = 13$ and $n = 55$) have zero energy ($E_{13} = E_0$; $E_{55} = E_0$); reproduced with permission from ref. [113].

Icosahedral structures of noble-gas clusters were actually observed experimentally in argon molecular beams.[114] There are contradictory speculations about their role in other situations, in particular, in seed formation for crystal growth.[28] A tempting but provocative hypothesis says that icosahedral growth is actually a dead end for crystal growth.

This picture of almost complete dominance of icosahedral structures appears to continue at least up to $n=250$,[89] perhaps even up to $n=309$[108]—but the LJ periodic crystal cannot contain fivefold rotation axes! In the experiment, it is actually fcc. This shows again the deficiencies of the LJ potential, because theoretical predictions of solid-state structure based on this potential arrive at the hcp form (hexagonal close-packed).[115] Not only the three-body terms missing in the LJ potential but also zero-point energy differences apparently lead to fcc rather than hcp[116] (even these calculations still have some model characteristics, since they are not completely ab initio and use some approximations). Therefore, there has to be a transition from icosahedral structures to fcc ones somewhere, perhaps with decahedral structures as intermediate stage. But that is already where our knowledge ends and speculations begin: from experiments, the transition is put somewhere in the range $n=750-800$,[114] while theoretical approaches point to the range $=1500-10000$[117] ($n=10179$ corresponds to an icosahedral cluster with 14 filled shells[19, 20]). Recent MD studies[118] try to model the transition explicitly dynamically, and claim better agreement with experiment by a dynamical coexistence of several (imperfect) structures.

Doye and Calvo[119] have pointed out that the exact positions of these structural transitions also depend on entropy, which can have different contributions to the Gibbs free energy of the different structural types. Therefore, part of the discrepancies between different experiments may be a result of different temperatures.

Alternative explanation attempts by faulted cluster models[26] at first appeared to provide a successful synthesis of fivefold centers and the fcc solid state, which also could have explained the advantage of fcc over hcp by preferential crystal growth into the fcc direction. But this could not be verified, on the contrary: the most recent modeling of the experimental data[120] are interpreted as proof for fcc, hcp, and rcp regions (random close packed) side by side in larger clusters in the experiments, in about equal amounts. This interpretation leads to the conclusion that these experimental systems (probably because of their preparation) cannot be used to study the transition from icosahedral structures to fcc.

In summary, LJ clusters are a seemingly trivial system which then turns out to be very complicated and exciting. The decisive size region of structural transitions is at rather large cluster sizes and hence difficult to reach with any of today's methods. Even the apparently simplest questions (which structure dominates for which reason in the solid state, and how do small clusters develop towards this structure?) are still wide open, in spite of frequent applications of many advanced techniques. This in some way simplest system is only of academic interest for most chemists. Therefore, these big gaps in our knowledge of this system show the limited abilities of our modern theoretical and experimental methods in this area, and this tells us to drastically lower our expectations for more complicated cases in "actual chemical applications".

3.2. Further Simple Systems

3.2.1. Non-Noble-Gas van der Waals Systems

The transition to fcc in other systems with van der Waals interactions (N_2, CO_2, etc.[121–123]) occurs at much smaller cluster sizes (e.g. about $n=30$). As an explanation, it is proposed that it is the anisotropy of molecular systems that leads to a generally larger strain. According to the analyses of Berry, Doye, and Wales[111, 112] strain increases with cluster size in icosahedral geometries, and larger anisotropies favor more densely packed geometries;[124] therefore, the transition from icosahedral to fcc geometries can be shifted to much smaller clusters. This tendency makes these systems much more amenable to theoretical approaches; so far, however, they have been much less investigated than the isotropic LJ system.

3.2.2. Morse Cluster

Variation of one further parameter, the width of the potential well in the pair interaction, leads from the LJ potential to the Morse potential (Figure 4). Global optimization studies of Morse clusters[125] arrive at the same basic structural types as mentioned above for LJ clusters, but there is a further complication: the structural type of the global minimum of smaller clusters does not depend solely on cluster size anymore, but can be changed by variation of the well width to any of the other structural types (Figure 5). This phenomenon can again be understood qualitatively with the above strain argument: variation of the well width directly changes the energy costs associated with deviations from the optimal pair distance, and thus also changes the contribution of strain energy to the total energy. Since the different structural types have different strain, the well width in turn influences the energy competition between these structural types.

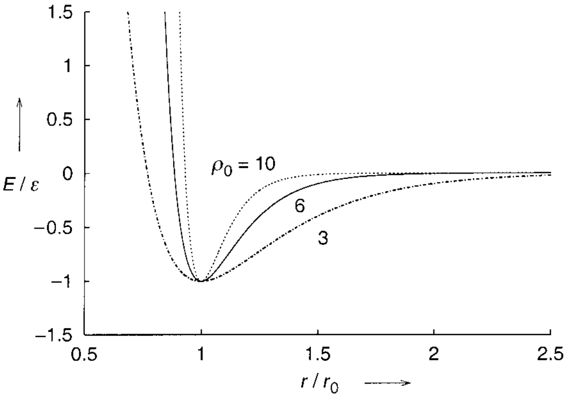


Figure 4. Variation of well width ρ_0 of the Morse potential (energy E in units of well depth ε as function of distance r in units of the equilibrium distance r_0); for $\rho_0 \approx 6$ the Morse and LJ potentials are the most similar.

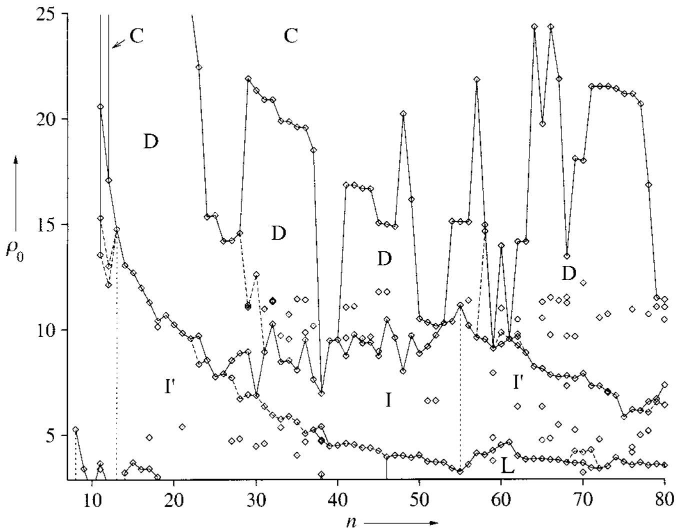


Figure 5. "Phase diagram" of Morse clusters: Change of structural type of the global minimum with cluster size n and with well width ρ_0 of the Morse potential (compare with Figure 4); abbreviations as in Figure 3; reproduced with permission from ref. [125].

3.3. Silicon Clusters

All the systems mentioned above are model systems with only simple pair interactions between the particles. The diversity of chemistry, however, is largely induced by more complicated interactions, which can be treated approximately by many-body terms, which lead to preferences for certain bond and dihedral angles. Accordingly, clusters of more realistic systems can be expected to exhibit other characteristic structures and other structural transitions. This behavior is shown for silicon clusters as one prominent example.

There has been experimental and theoretical interest in silicon clusters for quite some time; among others, Jarrold[126] and Smalley and co-workers[127] have offered reviews of this topic. Historically, small silicon clusters were first assumed to be simply pieces of the silicon crystal lattice. This notion was soon disproved by the observation of the surprisingly low reactivity of these particles,[17] which did not fit the common expectation (small particles have a larger surface area for their volume, and hence are more reactive). In this vein, attempts to construct structures for silicon clusters with similar surface reconstructions as bulk silicon[16] also turned out to be a misconception, since this cannot explain their reduced reactivity compared to the bulk.

After some dispute in the past, there is now good agreement between theory (QCISD/6-31G\ast level) and experiment (IR and Raman spectra) for the smallest clusters ($n \leq 7$).[128–131] Here we have agreement between experimental structures and theoretical global minimum energy structures. For larger clusters up to $n = 10$, there also appears to be agreement between various theoretical calculations with regard to the global minima. At $n = 10$ itself, the tetracapped trigonal prism (TTP) is now generally favored (Figure 6).[97, 132] This structure is unknown in the icosahedral growth pattern of LJ clusters, and also the smaller silicon clusters deviate from this pattern, with few exceptions, for example, the pentagonal bipyramid at $n = 7$.

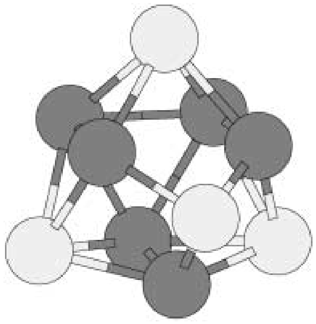


Figure 6. Global minimum of Si_{10}: tetracapped trigonal prism; the atoms at the corners of the trigonal prism are shown in dark, the capping atoms in light color.

For larger clusters, discrepancies set in. There is a large number of DFT studies with local minimization of guessed starting geometries,[16, 133] a dangerous way to proceed for clusters of this size (see Section 2.2). Probably more reliable are CPMD-SA studies,[134] but these were performed only for $n < 10$ and $n = 33,45$, without the interesting size region in-between. Other works used still less reliable treatments of the electronic problem (semiempirical methods, such as AM1[135] or "tight binding" (TB)[136–140]), but some of them did employ global geometry optimization.[139] The overall impression of these and many similar studies is that of differences between each other and to the experiment.[141]

The most prominent experiments in this area with nearly direct structural information in the size region $n > 12$ are mobility measurements of silicon clusters in helium gas.[142, 143] Comparison of the resulting data with trajectory calculations[144] or projection approximations of hard spheres allows the determination of the outer form of these clusters (but not of their inner structure). According to these results, clusters in the size region $10 \leq n \leq 20$ are not spherical but markedly prolate (elongated), in the region $24 \leq n \leq 28$ there is a structural transition with several coexisting forms, and still larger clusters are mostly near-spherical oblate.

These structural transitions are confirmed by a collection of experimental binding energies, indirectly deduced from several experiments in the size region $5 \leq n \leq 75$[145, 146] and directly measured by calorimetry[147, 148] in the region $65 \leq n \leq 890$. These data can be compiled into one single, consistent picture (Figure 7), which again shows this structural transition in the same size region.

Recently, by using a simple EA strategy directly on the DFT level in the size region $10 \leq n \leq 20$, Jarrold and co-workers[141] have found prolate cluster structures that agree with the experimental mobility data and feature TTP as basic building block. Figure 8 shows a typical member of this set of structures. These results were then confirmed in various ways: Jarrold's group investigated the energetics of various dissociation pathways[149, 150] and found consistency only for these new structures. Frauenheim and co-workers[94] applied a DFT-based TB scheme in a simplified EA structural optimization and arrived at qualitatively similar structures, with some quantitative improvements, but still in agreement with the

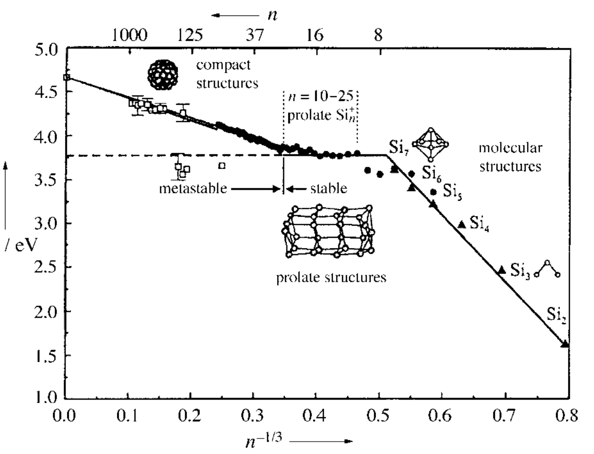


Figure 7. Binding energy per atom (E_b) of Si_n as function of cluster size (inverse cluster radius $= n^{-1/3}$); in this common axis scaling,[22] changes in trends are visible as changes in slope of linear fits; data of several experiments[145–148] are shown; reproduced with permission from ref. [148].

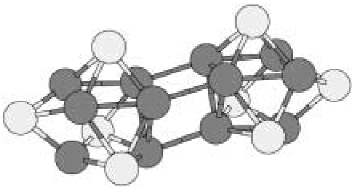


Figure 8. One proposed structure[141] for Si_{20}, build from two Si_{10} units in TTP form; colors of the atoms as in Figure 6.

mobility data. Now there are also spectroscopic measurements further confirming these structures.[151] This accumulated evidence suggests that we now "understand" this size region $10 \leq n \leq 20$.

Nevertheless, a few points still require clarification: the level of theory mostly used (DFT, or DFT-TB) is perhaps not sufficient; for some small clusters, DFT fails, and the energy differences between different isomers decrease with cluster size, so that small errors have a large effect. Furthermore, a general understanding beyond a black-box agreement between experimental and theoretical results seems to be lacking. For example, there is no explanation why TTP should be a good building block for larger clusters. TTP is one of the so-called "Bernal holes" in random close packings of hard spheres[18] and is perhaps also important in the seemingly completely different system Hg_n (Section 3.4); but why TTP is here (and perhaps in Hg_n) a particularly stable and preferential building block remains unclear.

If one concedes that the size region $10 \leq n \leq 20$ is nevertheless explained, there is still the region $24 \leq n \leq 28$ with the actual structural transition. The first investigations of this area have been made,[152] but only on the DFT-TB level, for a few selected cluster sizes ($n = 25,29,35$), and without direct comparison to the experimental mobility data. Future work still needs to explain why further metastable isomers are reproducibly observed far beyond the structural transition[147, 148] and which new structural principles come into effect at the structural transition: If TTP is still a good building block, how is the observed transition in the outer form of the clusters possible? Or, if TTP does not occur in larger clusters, why does it stop to be a good building block at these cluster sizes?

As a final remark it must be emphasized that there are big differences between silicon and carbon clusters[86, 137, 153, 154] (this will come as no surprise to inorganic chemists). Small carbon clusters are usually linear or circular; there are no such forms in Si_n. The existence and stability of fullerene-type structures for pure Si_n is still disputed, in spite of many studies on this topic;[155] current evidence is not favorable.

3.4. Mercury Clusters

Smallest clusters of metallic elements show no metallic properties; these set in only from a certain cluster size, depending on the element and on the property under study.[12, 22, 156]

An important example for this phenomenon is provided by mercury clusters.[157] Several experiments[158–166] indicate that there is a nonmetal–metal transition in mercury clusters, but the size range is disputed: theoretical estimates and experimental evidence vary between $20 \leq n \leq 70$,[159] $n \geq 100$,[160] and $n = 400$.[161]

Simple theoretical reasoning, highly accurate CCSD(T) calculations,[167] and experiments arrive at a very low binding energy and large atomic separation for Hg_2, underpinning its van der Waals character. Various experimental and theoretical details[160, 168] lead to the expectation that this character continues up to about $n = 13$. Approximately from this cluster size onwards, covalent character is expected, until the actual transition to the metal at still larger sizes. Hence, we have not one but two transitions in bonding character, and there should be some evidence for this also in the corresponding cluster structures.

There is, however, an acute lack of structural information from experiments. Some expensive theoretical calculations[169–171] relied on structural hypotheses derived from the above expectations; comparisons with experiment still leave some room for improvement. Less expensive studies with model Hamiltonians[172] or at the DFT level[173] can avoid structural hypotheses but are not sufficiently accurate; model Hamiltonians are based on assumptions of a certain bonding character, and DFT is known to be problematic for systems with long-range van der Waals type interactions.

Already at the smallest cluster sizes global minimizations on highly accurate ab initio levels are much too expensive for this system. Therefore, an ab initio/empirical hybrid model[171] was used in conjunction with the EA methods explained in Section 2.2 to arrive at global minimum energy structures[98] for Hg_n, $n = 7-14$. These structures deviate surprisingly strongly from the icosahedral growth scheme which should clearly be expected for a pure van der Waals system in this size region. Icosahedral structures can be found at some cluster sizes as high-energy local minima, but all global minima have completely different structures (Figure 9). At $n = 7$ and $n = 10$, structural and energetically particularly prominent clusters are found: in this hybrid model, Hg_7 has the astonishing structure of two tetrahedra joined at a common tip. Hg_{10} surprises by having qualitatively the same

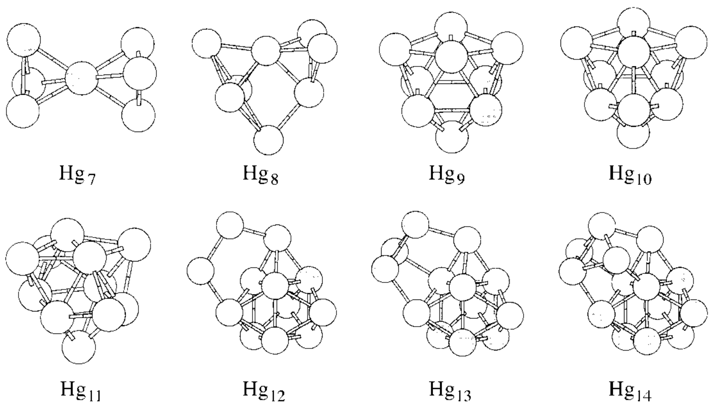


Figure 9. Proposed global minimum energy structures[98] for Hg_n, $n = 7-14$, in a quantum mechanical/empirical hybrid model; the icosahedral build up typical for van der Waals systems is not discernible, structures of this type are at best high-energy local minima (not shown here).

TTP structure as Si_{10}. There is no direct connection to experimental data yet, for example, in the form of calculated ionization potentials. Nevertheless, the special roles of $n = 7$ and $n = 10$ seem to be quite in agreement with experiment.[98] A closer examination of the published experimental data[158, 174] shifts the transition from van der Waals to covalent character (which was put at $n = 13$ largely because of the hypothetical icosahedral structure) to $n = 11$ (Figure 10). This again is in better agreement with the new structures, since after one further capping of the TTP structure at $n = 11$, a new geometric shell has to be established upon transition to $n = 12$. This hybrid model was tested only for very small mercury clusters. Currently, single point calculations for larger clusters are being carried out to check the model for larger clusters. In any case, the above findings indicate that the simple and obvious picture of a transition from van der Waals to covalent character at the first icosahedral shell closure ($n = 13$) is perhaps too simple. Even if the structures shown here are not fully correct, there is either no direct connection between bonding type and cluster structure, or the pure van der Waals character is already lost in very small clusters. Furthermore, a lot of theoretical development work still needs to be done before one can even start to think about investigation of the transition to the metal at still larger cluster sizes.

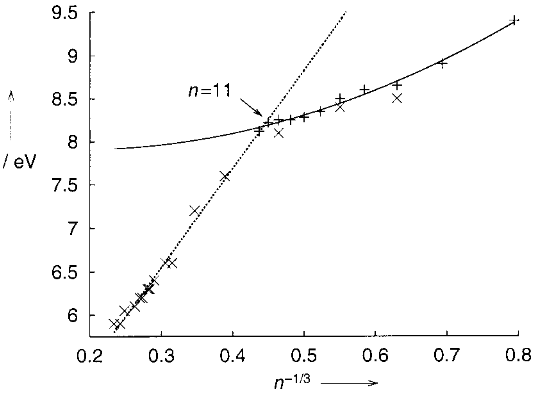


Figure 10. Trends in experimental ionization potentials E_i of Hg_n; data of several experiments (+: Cabaud et al.,[158] ×: Rademann[174]) are plotted as a function of cluster size (inverse cluster radius $= n^{-1/3}$), as well as a linear fit for the limit of large clusters and a quadratic fit in the region of small clusters. The transition between these two occurs close to $n = 11$.

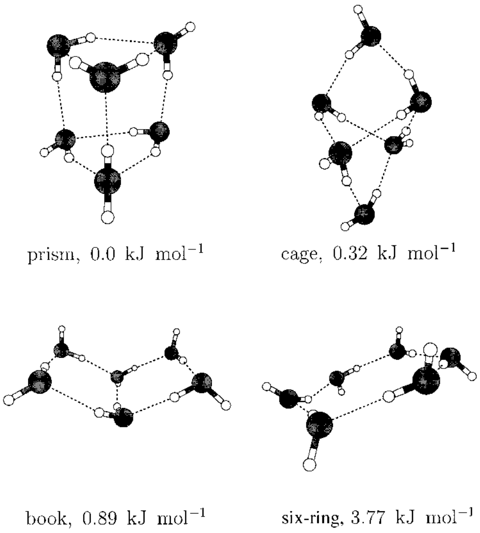
3.5. Pure Water Clusters

Pure water clusters were recently reviewed by Ludwig.[175] From the different point of view of the present article, to provide a transition to the following Section 3.6, and to supply a few additions, we want to consider these systems briefly.

The smallest clusters $(H_2O)_n$, $n = 2,3$, have been treated in a highly exact fashion by electronic structure theory[176–178] as well as by nuclear dynamcis calculations,[179] in excellent agreement with experimental results (ref. [180] older literature cited therein). From this, we know that the level of quantum mechanical treatment of the electronic structure should at least be MP2, pure HF calculations are not sufficient: the dimer interaction energy at HF level amounts to only $-14.85\,\text{kJ}\,\text{mol}^{-1}$; MP2 contributes a substantial addition of $-6.276\,\text{kJ}\,\text{mol}^{-1}$, whereas correlation contributions at still higher levels give only another $-0.21\,\text{kJ}\,\text{mol}^{-1}$.

Another lesson from these publications (as well as earlier ones in this area) is that it is very difficult (if not impossible[181]) to find an empirical potential that reproduces the properties of water in as diverse surroundings as clusters, fluids, and the solid state. Fitting a suitable functional form to the ab initio results mentioned above yields a potential that reproduces the tunneling splittings in the spectroscopic experiments mentioned above very well,[182] but this accuracy appears to be rather limited in configuration space: Simulations of liquid water with this potential result in pair distribution functions that deviate more from experimental results than those stemming from much simpler potentials, such as TIP4P.[183] Therefore, it seems more promising to build a potential on a much broader basis of ab initio data.[184]

For potentials as different as TIP4P[185, 186] and ab initio MP2,[99, 187] some cluster structures are nevertheless qualitatively the same: Small clusters up to $n = 5$ are rings, and larger clusters with $n \geq 7$ have three-dimensional structures. The necessary structural transition in-between seems to be very close to $n = 6$, and therefore we see a large structural diversity for the hexamer, with very small energy differences between qualitatively different isomers: at a temperature of absolute zero and without zero-point energy, the prism clearly has the lowest energy at any suitable ab initio level,[99, 187] followed by several variants of the cage. Quasiplanar structures as the book and the six-ring are still higher in energy (Figure 11). In the limited spectral region of the experiments by Saykally et al.,[188] only the cage form is found. Even if signatures of other forms may still hide in unexplored regions of the spectrum, the estimated temperature of the experiment (about 5 K) is consistent with the presence of just one isomer, in spite of the small energy differences. This discrepancy between theory and experiment seems to be removed by addition of zero-point energy corrections;[189] even if one fully trusts the empirical potential necessary to evaluate these corrections by quantum Monte Carlo (QMC) calculations



prism, 0.0 kJ mol^{-1} cage, 0.32 kJ mol^{-1}

book, 0.89 kJ mol^{-1} six-ring, 3.77 kJ mol^{-1}

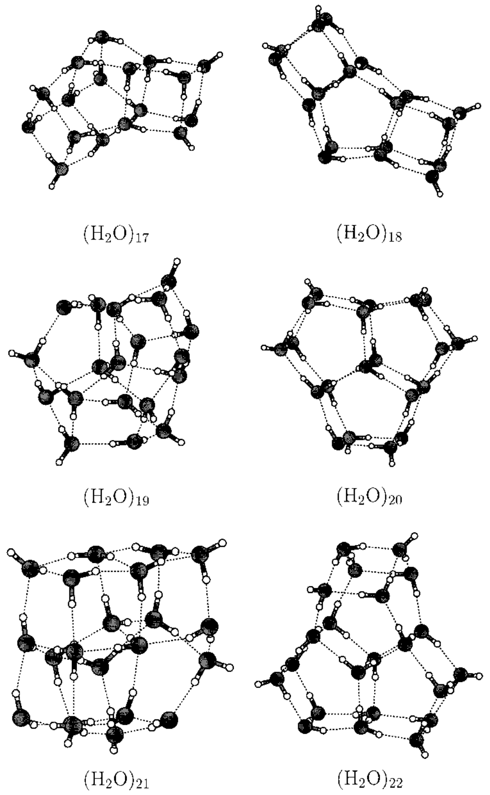
Figure 11. Global and local minimum energy structures of $(H_2O)_6$ at LMP2 level (Table 1) with an aug-cc-pVTZ basis set;[99] energies relative to the prism (without corrections for zero-point energy and finite temperatures).

(instead of a more exact ab initio surface), some doubt still remains, simply because the errors in the large zero-point energy corrections may be larger than the small energy differences of the isomers before and the still smaller energy differences after applying these corrections. Kim and Kim[187] have also claimed to get rid of this discrepancy with corrections for both zero-point energy and finite temperatures. But there are methodical problems also in this case, since the frequencies necessary for these corrections were calculated only in harmonic approximation, which is problematic for this system. Nauta and Miller[190] found only the planar six-ring and no trace of prism or cage for the water hexamer inside helium droplets. Therefore, at least for $n = 6$, the cluster structure actually found depends quite strongly on the preparation conditions, and this could be the case in Saykally's experiment, too. Hence, at this time we can only conclude that the exciting problem of the water hexamer is still an open one.

For somewhat larger clusters ($n = 7-10$), there is still fairly good agreement between theory (MP2 and empirical potentials, empirical but anharmonic simulation of spectra) and experimental OH stretch vibrational spectra.[191] Up to $n =$ 11,12, harmonic spectra at the MP2 level are available.[192] For still larger clusters, these approaches become too expensive.

On the very simple empirical TIP4P level, global minimum energy structures are known with a fair amount of security up to $n = 20$[185, 186] and with reasonable probability up to $n =$ 22.[186] Analysis of these global minima shows an almost complete lack of systematic structural buildup. At best, one can diagnose a preference for cubes and pentagonal prisms and structures assembled from these units, which is not quite in agreement with chemical intuition.

Surprisingly, one also finds that in all of these global minimum structures (with the sole exception of $n = 19$) all the water molecules are on the surface of the cluster (Figure 12). A transition to structures with inner water molecules obviously has to occur with increasing cluster size, but the critical size for this transition has not yet been located reliably.



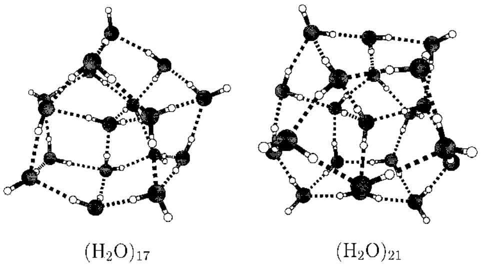
$(H_2O)_{17}$ $(H_2O)_{18}$

$(H_2O)_{19}$ $(H_2O)_{20}$

$(H_2O)_{21}$ $(H_2O)_{22}$

Figure 12. Global minimum energy structures[185, 186] of $(H_2O)_n$, $n = 17-22$, for the empirical TIP4P potential. For $n = 21$, one does not find a centered dodecahedron (cf. Figure 13) but again a structure assembled from (distorted) cubes and pentagonal prisms, with all the water molecules at the surface of the cluster.

Of course, TIP4P is an extremely simplified model. Global geometry optimizations[193] (massively parallel on a CrayT3E) on the sophisticated TTM2-F potential[194] (based on TTM2-*R*,[184] with flexible monomers, and a very good internal water potential with nonlinear dipole surface by Partridge and Schwenke[195]) confirm many but not all of these globally minimal TIP4P structures. Interestingly, deviating global minima are distinguished by a central water molecule; this happens for the first time at $n = 17$ (Figure 13). Again in contrast to the TIP4P results, we find for TTM2-F at $n = 21$ a (deformed) dodecahedral cage structure around a central water molecule. Both findings agree better with chemical



$(H_2O)_{17}$ $(H_2O)_{21}$

Figure 13. Global minimum energy structures[193] of $(H_2O)_n$, $n = 17$ and 21, for the ab initio adapted TTM2-F potential.[194] Already for $n = 17$, the best structure has one central water molecule, and for $n = 21$ we find a centered (distorted) dodecahedron; both findings are in contrast to the TIP4P case (cf. Figure 12).

intuition and with corresponding results for ion microsolvation clusters (Section 3.6). In any case, the exact location of this structural transition obviously depends strongly on the potential used. DFT and MP2 calculations as well as ab initio and empirical MD simulations are currently underway in our group, to further illuminate this problem.

Because of the very small energy differences between minimum structures of larger water clusters, corresponding to an easily changed hydrogen bonding network, the very notion of structure starts to become questionable, and only dynamical mean values from MD or MC simulations retain some meaning. This method does not fully contravene the above approach of quasistatic global geometry optimization. As already discussed in Section 2.2.3, we perceive these two approaches as complementary. Global geometry optimization yields the desired information on the underlying potential energy surface faster and more directly, and this permits a better assessment of the effects of different model potential terms. Even in the presence of nonclassical "smeared" structure distributions over whole regions of configuration space it is still interesting and useful to know the potential minima behind this distribution, be it only for a proper diagnosis and analysis of this situation. In spite of this objection, in my opinion, the attempts to capture properties of ice and water with special cluster models[196] for parts of the (dynamical) hydrogen bonding network are not misguided. Of particular interest here is the appearance of clathrate-like structures (Section 3.6), even if this is criticized by some authors.[197, 198] At least as useful, are the direct contacts between theory (with MD studies of large clusters of 1000 molecules, using empirical potentials and model-based simulation of IR spectra) and experiments on ice aerosols which are currently beginning.[199]

3.6. Ion Microsolvation Clusters

In this almost arbitrarily broad field, we only want to consider simple ions such as alkali cations and halogen anions with water as solvent, and we want to place the main focus on larger alkali cation water clusters.

Likewise, we will not attempt to give an overview of the extremely numerous experimental and theoretical studies on solvation in liquids. Nevertheless, some salient points of relevance here should be mentioned: recently, some experimental evidence on the reduced dynamics of hydrogen bonds in solvation shells of anions was published;[200] of course, this gives considerable support to the concept of gas-phase microsolvation clusters as models for bulk solvation in the liquid phase. Many studies agree in assigning different tendencies of ions, such as Na^+ to bulk and Cl^- to surface solvation; for example, this is observed in ab initio and DFT calculations,[201–203] in model potential studies of clusters,[204, 205] and MD slab calculations.[206] A consistent rationale of this observation apparently requires a combination of size and polarization effects.[204–206] Even ions of much closer chemical similarity, as Na^+ and K^+, have a different influence on the surrounding water ("structure-making" versus "structure-breaking"[207]). Finally, these systems even have some biological relevance: there is an X-ray structure of a cell membrane ion channel,[208] which differentiates between Na^+ and K^+ ions. The existence of this structure has intensified attempts to understand the mechanism of this selectivity. It does not come as a surprise that besides simple differences in ion size also the differences in solvation behavior could have some influence here.[209–213]

Microsolvation clusters in the gas phase (several reviews[214–217]) are often viewed as model systems for bulk solvation in the liquid phase. Obviously, there are some differences between these two situations, for example, in solvation clusters there are certainly surface artifacts, which are not present in the bulk solution. Also, exchange of solvent molecules may proceed in different ways in clusters and in the solution. Because of the experimental preparation conditions, the temperature region covered by clusters is presumably quite different (apparently below 150 K[218]). Nevertheless, microsolvation clusters in the gas phase are at least an important intermediate step on our way towards a better understanding of solvation in solutions, simply because they guarantee more closely controlled and less "averaged" conditions, which is advantageous for both experiment and theory.

Today, microsolvation clusters are experimentally accessible by various methods.[219–221] On the theoretical side, there are some ab initio studies of small clusters[222, 223] for the systems of interest here, $Na^+(H_2O)_n$, $n \leq 10$ and $K^+(OH)_n$, $n \leq 6$, and also comparisons between ab initio calculations, empirical potentials with and without polarization, and experiment.[224]

Of course, there are also very many studies of these microsolvation clusters with empirical potentials[225–227] (see also further citations in these articles), but considering the vast number of empirical water potentials we refrain from discussing them. The work with TIP4P/OPLS modeling discussed below of course is relatively crude, but they are at least partially justified by surprisingly good qualitative agreement with the ab initio calculations mentioned above and with MC results on more elaborate potentials.[228, 229] Among other things, experiments on solvation clusters of simple cations (the reviews cited above) also point to several magic numbers. One particularly outstanding item is the hypothesis of a dodecahedral clathrate cage of 20 water molecules around the central cation, independent of the type of this cation. This hypothesis is often ascribed to Castleman and Holland[230] but its roots can be traced further back in the literature.[231] Cage structures of this type but typically around hydrophobic guest molecules have been known for a long time as clathrate hydrates in the solid state. They occur in many natural and industrial situations[232, 233] and are examined theoretically (ref. [234] and literature cited therein) as well as experimentally (refs. [235, 236] and references therein). Combustion of methane from deep-sea methane hydrates is currently being considered as a new source of energy.[237, 238]

The casual naturalness of the clathrate hypothesis may have furthered its rather uncritical use as ad hoc structure hypothesis not only in microsolvation (from ab initio calculations[239] all the way to experiments[219, 220, 240, 241]), but also for the so-called "hydrophobic solvation" in the liquid phase, with questionable success.[197, 198, 242] Here, we are mainly interested in the experimental observation that $n = 20$ is a magic number for K^+ and Cs^+ ions but not for Na^+ ions, which is not immediately clear from the clathrate hypothesis.

A global geometry optimization study by Hodges and Wales[243] on several empirical potentials verifies the clathrate hypothesis for H_3O^+ as the cation—however, with the cation not in the center but in the cage periphery. Ab initio calculations[244] confirm this, recently also for NH_4^+ ions but again with slight modifications.[245]

Systematic global optimization calculations[221, 246] on the TIP4P/OPLS level confirm the ion-centered clathrate (with some modifications and refinements, see below) also for K^+ and Cs^+ ions, but they also show why Na^+ ions are different:[221] there, an unexpected structural transition was found between $n = 17$ and $n = 18$, from cation-centered structures to geometries with the cation placed far off-center (Figure 14). A detailed analysis of different pair interaction contributions and energy partitionings leads to a qualitative understanding of this transition.[221] This off-center structural type also dominates for $n = 20$, and it is not consistent with a dodecahedron—even if the dodecahedron would have the cation in the periphery, because the Na^+–water pair interaction is much too strong compared to water–water interactions to permit the concomitant partial loss of first-shell water molecules from the Na^+ ion (Figure 15). This structural transition appears to correlate with experimental results.[221] Of course, the theoretical finding that $n = 20$ is structurally not special at all in $Na^+(H_2O)_n$, is also in agreement with the experimental findings[220] and in contrast to the corresponding K^+ and Cs^+ ion clusters where $n = 20$ is a magic number.

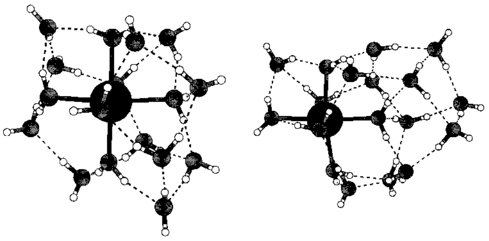
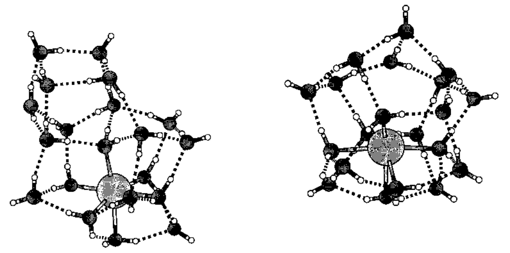
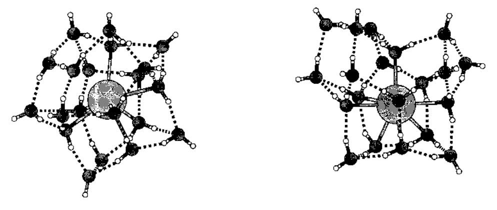

$Na^+(H_2O)_{17}$ $Na^+(H_2O)_{18}$

Figure 14. Global minimum energy structures[221] of $Na^+(H_2O)_n$, $n = 17$ and 18, for the empirical TIP4P/OPLS model. For $n \leq 17$, the Na^+ ion is at the center of the cluster, whereas it is strongly off-center for $n \geq 18$; this is in agreement with experimental observations.[221]


Na^+, global, 1214.47 kJ mol^{-1} Na^+, local, 1201.77 kJ mol^{-1}


K^+, global, 1155.24 kJ mol^{-1} K^+, local, 1151.90 kJ mol^{-1}

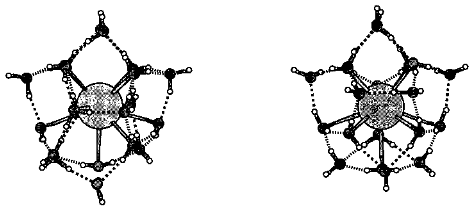

Cs^+, global, 1098.77 kJ mol^{-1} Cs^+, local, 1097.89 kJ mol^{-1}

Figure 15. Global and local minimum energy structures[246] of $M^+(H_2O)_{20}$, M = Na,K,Cs, for the empirical TIP4P/OPLS model. For M = Na, the global minimum is not a cage and not ion centered, the best (distorted) dodecahedral cage structure is also not ion centered and energetically clearly disfavored. For M = K,Cs, distorted dodecahedral cages are formally the global minima, but qualitatively different structures are local minima with almost the same energy (not a cage for M = K, and not only five-rings for M = Cs).

These results also show that even for K^+ and Cs^+ ions the picture of an ideal dodecahedral clathrate cage for $n = 20$ is too much of a simplification[246] (Figure 15). In both cases, the cage hull is heavily puckered and distorted, compared to the ideal dodecahedron. For the K^+ ion there are noncage structures very close in energy; and for Cs^+ ions, cages containing also four-rings and six-rings are very close in energy to the pure five-ring cage. Calculations at better levels of theory (also including temperature effects (entropy)) for this structural transition in the Na^+ ion case and for the various cage structures of alkali cations are currently being performed in our group.

Above, we mentioned that anions such as Cl^- or larger cations such as Cs^+ exhibit a tendency for surface solvation in theory and experiment, even in the smallest clusters, while other cations such as Na^+ prefer centered structures.[222] Part of this phenomenon is simply a result of to ion size. For the alkali cations,[221, 246] where the polarizability of the cation is not important,[224] already the simple TIP4P/OPLS model (without explicit polarizabilities) reproduces this behavior: the Na^+ ion does not show any surface solvation structures. Some of the corresponding K^+ ion solvation cluster structures are already more closely related to the Cs^+ ion cluster. In the Cs^+ ion clusters the Cs^+ ion itself is at the surface of such clusters, even for very small cluster sizes, and is completely enclosed by a solvent hull only at size $n = 18$, shortly before the occurrence of the distorted dodecahedral "clathrate" cage at $n = 20$. Figure 16 indicates these effects, by comparing the global minimum energy structures of these cation microsolvation clusters for $n = 4$. This phenomenon can be described as a structural transition from ion-centered forms to surface forms, with increasing ion size. For halogen anions[201, 203, 204, 247–250] it is tempting to draw a similar conclusion, since Cl^- and larger anions clearly prefer surface solvation, whereas centered structures can compete with surface structures only for the smaller F^- ion. The cited

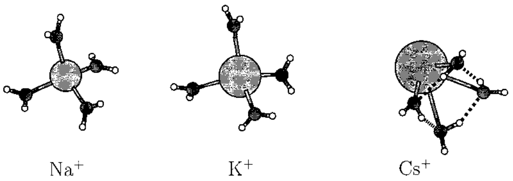


Figure 16. Global minimum energy structures[246] of $M^+(H_2O)_4$, M = Na,K,Cs, for the empirical TIP4P/OPLS model. For M = Na,K, the clusters are ion centered, for M = Cs the structure corresponds to surface solvation. For larger clusters, some best M = K structures have more similarity with the corresponding M = Cs structures.

sources agree, however, in ascribing this effect not just to the size of the ion but also to its polarizability (which is also related to the size).

4. Summary and Conclusions

In this article, several different cluster systems were presented. For each of these systems, characteristic transitions in structure (and other properties) as a function of cluster size (and also as a function of other factors) were diagnosed: Already for the simplest possible system, the LJ clusters, there is a surprising variety of structures, with (at least?) four different basic structural types, which are in close competition. For small and medium-sized LJ clusters, amenable to global geometry and MD or MC treatments, the icosahedral form wins almost always (except for very few isolated cluster sizes, between geometrical shell closures), as expected from the simple packing argument. From this trend, one can tentatively conclude that the deviation from hard-sphere behavior described by the LJ potential still is a relatively small perturbation. Icosahedral order, however, cannot survive all the way to the periodic crystal; this can be shown by the impossibility of fivefold rotation axes in the crystal, but also by alluding to different strains found for the different structural types (that is, with pair distances deviating from the minimum of the pair potential, induced initially by the "frustration" of the system in three-dimensional space). As yet this is only a qualitative description that does not permit predictions of cluster sizes where structural transitions actually occur. Strain in this classical LJ system is relatively small; thus the transition away from icosahedral structures occurs at clusters of such a large size that it could not yet be located reliably, neither by global geometry optimizations nor by MD or MC simulations. The higher strain in molecular van der Waals clusters, however, shifts this transition to much smaller cluster sizes which can be treated by these methods. If one varies the well width of the LJ potential (for example by substituting it with a Morse potential with different width parameter) but still stays with simple pair potentials of this general form, the basic structural types do not change, but the dominance of the icosahedral form can be lost completely by suitable choices of the well width. This result can again be understood by a strain argument: variation of the well width is nothing but variation of the energy difference to the pair potential minimum at a given deviation from the optimal pair distance. This, in turn, is nothing but a variation of the size of the contribution of strain energy to the total energy, and this leads to different preferences for the different structural types, because of their different strain.

Upon leaving such simple prototypical clusters for more "chemical" systems—silicon was taken as example in this article—isotropic pair interactions cease to be a good approximation; many-body terms have to be added to describe directed covalent bonds or preferences for planarity. Clearly, this leads to new structures that cannot be explained by simple packing or strain arguments anymore. Nonetheless we again do not find just one dominating cluster structure but structural transitions as a function of cluster size. For a few systems it has been possible to arrive at a well-founded set of simple rules to describe and perhaps even understand the various possible cluster structures, as was demonstrated for phosphorus by Marco Häser and Stephan Böcker.[251] However, these remain isolated islands of understanding; others will be added in the future. System-independent general rules would be still more interesting, but we do not yet see the beginning of a development in this direction.

Another possible parameter to vary is the type of chemical bonding. As shown here for the example of mercury clusters, there are links between cluster size, bonding character, and cluster structure. But actual structures found seem to be more complicated than expected from the current picture of changes of bonding character with cluster size. For clusters of relevant size, the highly accurate ab initio calculations and global geometry optimizations or MD/MC simulations necessary for a better understanding are still too expensive, even today.

The transition from atomic to molecular clusters is not trivial, since the difficult problem of an exponentially increasing configuration space of particle positions in the cluster is augmented by an also exponentially increasing search space of particle orientations. "Steps" (in iterative optimizations, or in MD/MC simulations) in these two spaces have a strong influence on each other, thus these two spaces are not separable. Therefore, it comes as no surprise that the cluster size region amenable to theoretical treatment of molecular clusters is about one order of magnitude smaller than that of atomic clusters. Nevertheless, in some cases it was possible to find characteristic structural transitions even in such a reduced size region, for example, in the system of pure, neutral water clusters the theoretically and experimentally fairly well investigated transition from quasiplanar to three-dimensional structures near $n = 6$ or the currently neither theoretically nor experimentally locatable transition from all-surface structures to clusters with at least one molecule in the interior. To a much larger degree than for the transitions mentioned above, it is immediately clear here that these structural transitions have to occur; but a more detailed understanding of the actual reasons for occurrence of these transitions at certain cluster sizes is still lacking completely.

As a final source of complication, we mentioned heterogeneous clusters, consisting of more than one species. Clearly, we have still more parameters to vary here, namely the relative distribution of the species in the cluster and the relative properties of the species (size, charge, polarizability, etc.). Changes in these parameters can again induce characteristic structural transitions in these clusters, as was demonstrated here with microhydration clusters of simple ions as an example. Again, also in this area, investigations are just starting.

Even if structural transitions in clusters are the rule rather than the exception (and perhaps even have to occur), and even if some structures appear in seemingly different systems (for example, icosahedral forms in van der Waals clusters and metals, or the tetracapped trigonal prism for Si_n and Hg_n), most of the basic questions mentioned in the introduction are still unanswered: Do structural transitions occur according to universal laws, or do they solely depend on the particular system (or potential)? One type of universal law has been known for a long time, namely the simple packing argument (at the level of hard spheres), and the strain argument for LJ clusters may turn into another universal law for van der Waals systems. But we still do not even begin to understand how packing, strain, and potential interact for more complicated potential forms (for example, with directed covalent terms) and what happens if the balance between these factors is changed. Clearly, we are still in a phase of accumulating empirical details and observations for various systems, as also done in this article.

Therefore, many old, basic questions are still open, for example, which potential form leads to which cluster structures and structural transitions? How can one deduce interactions between particles from experimentally observed structures and structural transitions (and perhaps magic numbers)? In a recent publication,[252] new universal connections between the potential surface and the potential function were discovered by catastrophe theory, but we still have a long way to go before we can answer these questions for clusters.

In a similar way, the connections of this field to its immediate neighbors also need further investigation. What is the actual importance of the largely static diagnoses of cluster structure transitions made here for the dynamics of cluster growth and for seed growth in crystal formation? Can we expect complete changes of cluster structure at structural transition sizes, or are seemingly optimal small seeds always dead ends because of their ultimately wrong structure, and the successful seeds are those that start their growth already in the correct bulk structure? Or is all this too idealized anyway, and seeds with a wrong structure end up as faults in the crystal?

Increasing computer power and more efficient implementations of theoretical approaches will permit simulations of structural transitions in clusters with an increasing amount of detail, in my opinion this will not necessarily also lead to understanding. This general problem also occurs in many other realizations of many-body problems in the natural sciences, for example in weather prediction, traffic dynamics, or in artificial and natural neural networks (brains). A detailed description on a microscopic level has become possible, but the actual many-body phenomena still seem elusive, because our understanding has to occur on a less detailed level. From this, it follows that we may have a better chance to increase our understanding if we manage to introduce intermediate levels with less detailed descriptions. In the cluster structure problem discussed here, one possible candidate could be a suitably generalized three-dimensional packing problem, with larger and partially flexible building blocks, the inner properties of which are determined in advance by (ab initio) calculations but then neglected.

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