The Physics of Small Clusters

Recent Advances in the Theoretical and Experimental Approach

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Small atomic clusters offer a remarkable example of interdisciplinary interest, since they are relevant to topics as diverse as crystal growth, catalysis and the photographic process as well as to 'astrophysical' chemistry. Lately, cluster physics has been a source of inspiration also for nuclear physicists. Only recently, however, has the physics and chemistry of small clusters been recognized as an independent subject, with its own new complex and unanswered questions, distinct both from the field of molecular physics and from that of solid state physics.

The great step forward in the research on clusters sprang from the possibility of preparing and probing 'free' and 'size-selected' aggregates of a large variety of elements. While alkali metals, alkali halides and rare-gas microclusters have been investigated for a number of years, clusters of technologically important elements such as silicon, carbon and iron have been synthetized only during the past five years or so. This big advance must be credited to Richard Smalley and his collaborators at Rice University, Houston, Texas, who introduced a new cluster source which makes use of a pulsed laser beam for the vaporization of refractory elements. Similar sources have since been installed in a number of research laboratories in the United States and more recently in Europe.

Here, we shall focus on some aspects of the physics of 'free' microclusters, in particular on the study of the electronic and structural properties of different sized aggregates where the number of atoms n ranges from 2 to $\cong$ 100. Our aim will be to point out the major achievements as well as the major open questions. For references to specific work we refer the reader to the proceedings of recent symposia and to a recent book [1]. (Specific reference will be made only when the work is not included in Reference 1.)

Structural Characteristics

The most widely known aspect of clusters is the existence of special sizes at which high peaks in the mass distribution are observed, the so-called 'magic numbers'. Their value depends strongly on the material and seems to be characteristic of the type of bonding. Magic numbers raise the complex question of the stability of microclusters for which no comprehensive approach exists. A fairly satisfactory explanation has been given for the alkali metals based on a simple jellium-shell model (introduced by Walter Knight, Marvin Cohen and co-workers at the University of California, Berkeley), and for rare gases and alkali halide clusters where structural factors are decisive. With semiconductor and non-simple metal clusters, the criteria seem to be more complex owing to the strong correlation between electronic structure and geometry. For these systems, the use of classical potentials, borrowed from previous work on the corresponding homogeneous systems, is bound to lead to rather inaccurate computations, since the smallness of the system dramatically changes the nature of the chemical bonding. Theoretical work based on *ab-initio* methods is needed.

Most of the effort in this area has so far focussed on the search for the equilibrium structures. Because of the complexity of the potential-energy surface of an aggregate of $n > 3$ atoms, Monte-Carlo and molecular dynamics techniques appear to be necessary for a reasonable sampling of the possible low-energy configurations. Particularly useful has proved to be the Car-Parrinello method (*ab-initio* molecular dynamics) [2], which combines the advantages of molecular dynamics sampling with the accuracy of the local-density-functional approach to the study of chemical bonding. Energy minimization is carried out by simulated annealing strategies and unforeseen structures of relatively low energy have been discovered for silicon, germanium, sulphur, selenium, sodium and gallium arsenide microclusters of up to 20 atoms.

In spite of the intrinsic difficulty of finding the global minimum, the theoretical approach to the study of structural properties is at a relatively advanced stage for a number of materials. Experimental information, however, is rather limited despite the progress that has been made in performing in-beam studies [3]. Although a free cluster offers obvious advantages in comparison to a cluster deposited on a substrate, no direct investigation of the geometry of an in-beam cluster seems possible. On the other hand, such measurements have been made on deposited (metal and semiconductor) aggregates with high resolution electron microscopy, X-ray or electron diffraction, and extended X-ray absorption fine-structure (EXAFS) measurements, and more recently with scanning tunnelling microscopy. This latter technique is particularly promising for very small clusters. Indirect information can also be obtained from spectroscopic studies. Only recently has the (Jahn-Teller distorted) ground state geometry of Na_3 been unravelled using depletion spectroscopy by stimulated emission [4]. Other remarkable work has been done on Cu_3 employing fluorescence, and on the excited electronic states of some trimers (Li, Na, Cu, Ag, Al) with resonance enhanced multiphoton ionization. These spectroscopic studies, however, cannot be easily extended to larger clusters, since the high density of the excited electronic states results in highly congested spectra and in short lifetimes for the intermediate state. A promising direct structural tool is a technique which grew up in nuclear physics and makes use of the ''Coulomb explosion'' of highly charged clusters (Coulomb explosion imaging). So far, results have been published on C_3 and C_4. In particular, a ring structure has been established for C_4 which is in conflict with the linear structure suggested by calculations and photoelectron spectroscopy; the situation is not fully understood.

Temperature Dependence

As far as stability is concerned, the first natural question is the extent of temperature effects on electronic and structural properties. Again, this is a realm where computer simulations can

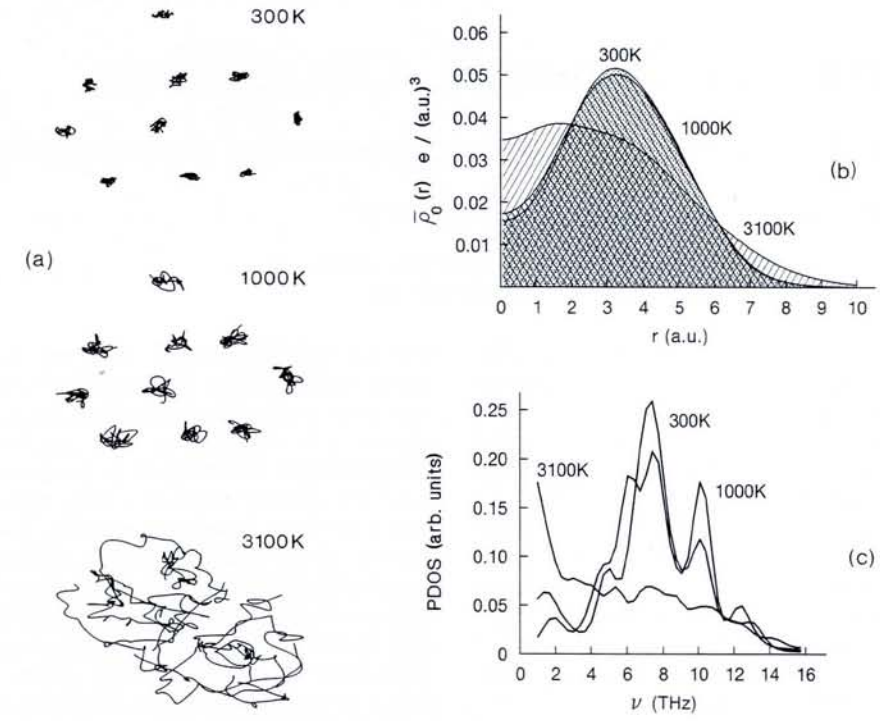

Fig. 1 — Si_{10}: results of ab-initio MD at different temperatures (from Ref. 5). a) a planar projection of the atomic trajectories, b) spherically averaged distribution of the electron density, c) density of vibrational states.

provide some insight, while experiment cannot yet assess the effective internal temperature of a cluster of $n > 3$. For instance, *ab-initio* molecular dynamics simulations at finite temperature (see also [5]) show that the 10-atom silicon cluster (a magic number for silicon) is very stable, in so far as structural, vibrational and electronic properties are concerned, up to temperatures where the cluster is 'melted'. This is illustrated in Fig. 1. *Ab-initio* molecular dynamics shows also that, owing to the flatness of the potential energy surface, temperature effects on sodium clusters are important at relatively low temperatures (even below room temperature).

The lack of control of the effective internal temperature of a free cluster hampers also the experimental investigation of one of the most fascinating questions: the melting transition and its size dependence. In a small aggregate of say ten atoms, it is not evident what melting means. Very detailed molecular dynamics studies on rare gases show that there is a range of temperatures where the cluster fluctuates between a solid-like and a liquid-like phase (phase co-existence). Experimental effort has concentrated on monitoring some parameters which could show a kind of molten or diffusive state of weakly bound clusters, by doing electronic and vibrational spectroscopy on the host molecules. The size dependence of band positions, widths and shapes exhibits abrupt changes, although their interpretation in terms of a melting transition is not clear, since *e.g.* isomerization would produce similar effects. The dependence on size of the melting temperature of large supported gold clusters was investigated in a classic experiment by Buffat and Borel 13 years ago. Only very recently, have Ercolessi *et al.* [6] performed classical molecular dynamics simulations of (free) gold clusters with n = 200-900 and gained insight into the melting mechanism and its size dependence.

Transition to Homogeneous System

Free clusters open up the possibility of studying how the properties of a homogeneous system develop from those of a small agglomerate of atoms. One interesting and open question is: How many atoms are necessary before the crystal structure establishes itself? Recently, there has been much discussion of the case of silicon — with different theoretical models giving widely differing predictions (ranging from 20 to ≅ 1000 atoms). *Ab-initio* calculations using the Car-Parrinello method have so far been performed for silicon clusters up to 40 atoms which indicate that the onset of the diamond structure is still far away [5]. In the case of rare gases, where size effects are expected to be much less dramatic than in silicon, the magic numbers observed in free jets of Ar, Kr and Xe reveal the presence of non-crystalline shapes (with five-fold symmetry) up to ≅ 1000 atoms [7].

Size trends in the excitation spectra and the establishment of the energy gaps of semiconductors and insulators are also under study. A remarkable result has recently been published on the rare gases, where the fluorescence excitation spectrum has been measured from the atom to aggregates of ≅ 3000 atoms [8]. Fig. 2 shows how the electronic excitation spectrum evolves from the atomic spin-orbit split lowest excited state ($4p^5 5s \leftarrow 4p^6$) into surface excitons and finally, for $n \sim 2700$ into the longitudinal and transverse bulk excitons.

In the search for the emergence of the properties of the homogeneous system with increasing size of cluster, one important question is: How many atoms make a metal? The standard criterion for the definition of a metal concerns the spacing of the electronic levels at the Fermi energy which must be smaller than kT. This, however, is hard to test experimentally, especially in view of the fact that it is not possible to measure the effective internal temperature of the clusters. Calculations indicate that at least for the simple and noble metals, the metallic-type of bonding, interpreted as the 'delocalized

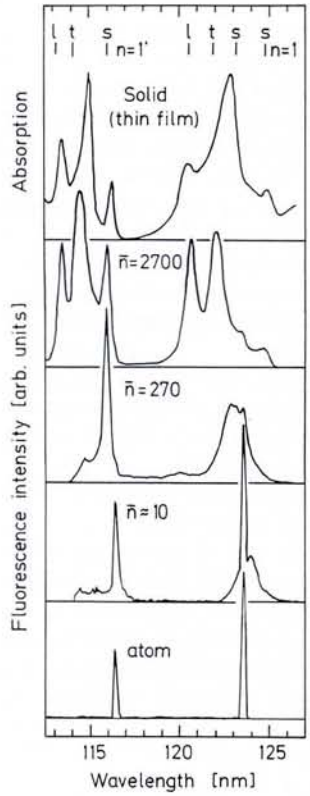

Fig. 2 — Fluorescence excitation spectrum of a krypton cluster beam for different average cluster sizes $\bar{n}$, estimated from the expansion conditions. (Adapted from Ref. 8).

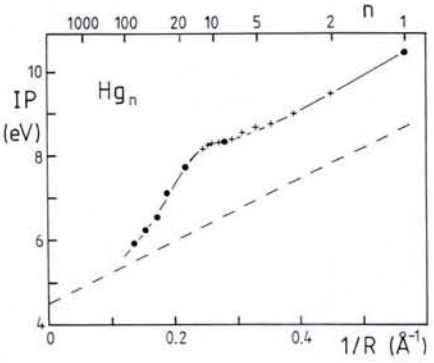

Fig. 3 — Ionization potential of Hg_n versus reciprocal cluster radius R (calculated from n and the bulk average density). The dashed line represents the classical behaviour of metallic Hg droplets. (Adapted from Ref. 9).

nature of the electron states' persists down to very small sizes. This is naturally reflected in the success of the jellium-shell model to interpret magic numbers. Moreover, sodium clusters with as few as eight atoms are found to behave as metallic droplets in photoabsorption measurements made in the visible range. Their response is dominated by plasma resonances whose frequencies and lineshapes are well accounted for by ellipsoidal-jellium-models. Even more interestingly, experimentalists have tried to detect the non-metal-metal transition in the variation of measurable quantities such as the ionization potential (IP). Success has been achieved in the case of mercury clusters, where a spectacular variation of the slope of the IP curve *versus* cluster 'radius' has been observed (Fig. 3, [9]). The slope anomaly has been interpreted as marking the onset of a gradual transition from the van-der-Waals ($n \leq 13$) to the metallic type of bonding ($n \geq 100$). Support for this interpretation comes from the observed changes in the auto-ionization features of the ion yield, due to excitation of electrons from 5d states: From an excitonic-type of behaviour for $n < 12$, they gradually broaden in the range from $n = 13$ to $n = 20$, at which size the onset of the 'bulk-like' behaviour is identified. Another interesting way of looking at the non-metal-metal transition was introduced by Di Cenzo *et al.* [10] and applied to mass-selected clusters of gold deposited on amorphous carbon. The parameter they looked at is the core-level shift measured in photoemission (XPS) as a function of size, with the idea that its appearance for the small clusters reflects the suppression of metallic screening. This indicates that gold clusters of ≅ 150 atoms are still 'not fully metallic'. The relevance of this result for free clusters is not clear yet owing to the fact that the influence of the support is not known.

Intrinsic Electronic Properties

We now turn from the question of how the electronic properties of the solid are built up with increasing number of atoms, to the intrinsic electronic properties of the small clusters themselves. Particularly impressive in this regard are the results from photoelectron spectroscopy of free and mass selected anions. The spectra (reported so far for alkali metals, Al, the IVa-elements, Cu, Ag, Ni, and a few weakly bound systems) refer to energies close to the Fermi energy. They provide an estimate of the electron affinities (EA) and of the energy gaps of the corresponding neutral clusters. Notable conclusions from these studies have so far been the following:

i) In agreement with measurements of the ionization potentials (IP), the electron affinities of one-electron metals show that there is an alternating character of even and odd sized clusters, and for even n the system is electronically 'happier' (lower EA and higher IP).

ii) Relatively large energy gaps and low EAs belong to sizes which largely correspond to the magic numbers observed in the abundance spectra. Two good examples are copper where these are again the magic numbers of the jellim-shell model, and carbon for which the 60-atom cluster is spectacularly distinct from the others in the range n = 48-84.

iii) C_n^- aggregates reveal pronounced odd-even alternations, which abruptly invert at $n = 10$. One possible interpretation associates it with a structural change (from chains to rings).

With surface chemistry much in mind, a great deal of effort has been directed to the measurement of the chemical reactivity of small free clusters. One notable example in semiconductor cluster chemistry is the detailed investigation carried out on reactions relevant to silicon deposition and etching (*e.g.* of Si^+ with silane and of Si_n^+ (n up to 6) with F). A larger number of experimental results refer to transition metal microclusters, which offer the natural intermediate towards the study of heterogeneous catalysis at a microscopic level. This research has been sparked by early findings on H chemisorption on Co_n and Fe_n which clearly showed a dramatic size depen-

dence of the reactivity. Also, the anti-correlation between maxima in reactivity and minima in ionization potential curves, found for some systems, ($Fe+H_2$, $Nb+H_2$, $Nb+N_2$), indicated that a simple charge transfer model could explain it. This however does not seem to be general. More recent detailed experiments on chemisorptive systems, such as H_2+NH_3 on Fe_n and O_2 on Al_n^+, indicate that the interpretation of the products of a chemisorption process can be rather delicate. Lack of theoretical approaches in this field is manifest and contrasts with the growth of experimental data.

Finally, we mention a topic where theory and experiment are progressing in parallel and which is very specific to insulating clusters: the nature of the states occupied by excess electrons. The interest resides in the fact that this can be different from the bulk. For instance, in polar bulk media (H_2O, NH_3) the electron becomes self-trapped (small polaron), while for small clusters, a diffuse surface state is likely to offer the only bound state. In alkali halide clusters, an excess electron could be localized either on a specific alkali cation or at a lattice site normally occupied by a halide ion (F-centre) or could reside in an extended surface state. The nature of the most favourable state is expected to depend crucially on cluster size and stoichiometry. Electron attachment, detachment, photoelectron spectroscopy, and dissociation spectroscopy are being employed to characterize these systems.

Although we have not been able to cover all the exciting current studies on clusters, we believe that we have given an idea of the richness of the field and of the variety of the methods which have allowed (or will allow) progress to be made.

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Amsterdam Pulse Stretcher on its Way

While the bicentennial of the French Revolution was being commemorated in Paris, on 14 July, physicists in Amsterdam were celebrating the formal start of construction of the new Amsterdam Pulse Stretcher (AmPS) at NIKHEF. The ground-breaking ceremony, conducted by B. Veltma, member of the board of the Nethelands' organization for Scientific Research (NWO), involved driving a concrete pile 18 m long into the ground.

AmPS is essentially a storage ring 212 m round which will be used in conjunction with the existing medium energy accelerator (MEA) at NIKHEF to provide the experimenters with "continuous wave" electron beams at energies up to 900 MeV. The duty factor will be 90% compared with 1% at present and a maximum energy of 550 MeV.

The electron beam can either be extracted from the ring and used in the existing experimental hall for high-resolution coincidence studies or it can be stored in the ring for use with an internal target. In such experiments the electrons interact with target nuclei in a rarefied (possibly polarized) gas stream. A new dedicated experimental hall is being built for this type of experiment. The new facility will be used to study the properties of nucleons in atomic nuclei, and especially the interaction between nucleons at short distances and the role of the first excited state of the nucleon, the delta.

The civil construction of AmPS will be finished next year, the installation of the ring first tests are scheduled for 1991, with commissioning in 1992.

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ATMOSPHERICS

In all sorts of communities, the state of the upper atmosphere is becoming the number one worry. At a meeting of the European Ecumenical Council held in Basel in May on the theme "Peace with Justice" a group of 17 physicists led by the Energy Working Group of the German Physical Society and including eastern European colleagues went so far as to present a manifesto in which they recommended *inter alia* reducing the consumption of fossil fuels in Europe by a factor of 3 1/2 over the next 25 years. The full text of the manifesto is published in *Physikalische Blätter* **45** (1989) 8, p. 340 and an English translation in available from Prof. K. Schultze at RWTH, Aachen. The CNRS in the latest issue of *Nouvelles des Presses du CNRS* announces publication of a book at 150 FF by Marcel Nicolet on *Ozone, l'Equilibre Rompu* in which the author makes a real attempt to collate the information that is available and assess how much is known about this hugely complex system that is the biosphere. The Swiss Physical Society has also just produced a booklet *Vom Menschen verursachte Klimaveränderungen* which gives a lot of data on energy balances, CO_2 measurements, temperature records and so on concluding with a bibliography of recent relevant literature. This is available from the Society on request.

Meanwhile governments at the highest level are studying the data and possible scenarios. The Intergovernmental Panel on Climatic Change set up about a year ago held its second session in Nairobi in June and the report of this was to be out by the end of September. The full assessment report is scheduled for 1990. The Executive Council of the World Meteorological Office meeting also in June was particularly concerned with possible climatic changes, but then so too was the UN Governing Council of the Environmental Programme and most international bodies like FAO have their specialist groups.

Finland to Join CERN

Finland has opened negotiations with CERN with a view to its becoming a full member after a transitional period of a few years. Based on its net national income Finland will be required to pay some 1.9% of the overall annual budget presently running at about 825 MSFR. Finnish physicists have for a number of years participated in experiments at CERN and have lately taken part in the design of Delphi, one of the four LEP experiments.