The science of clusters: An emerging field

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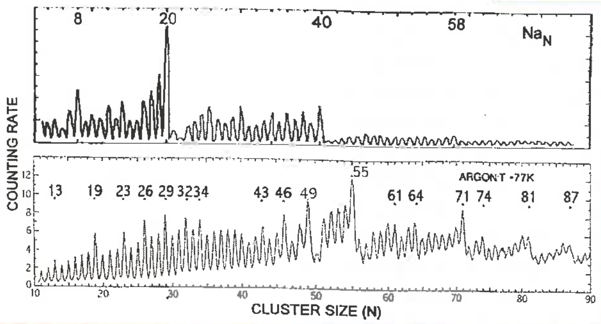
A group of atoms bound together by interatomic forces is called an atomic cluster (AC). There is no qualitative distinction between small ACs and molecules. However, as the number of atoms in the system increases, ACs acquire more and more specific properties making them unique physical objects different from both single molecules and from the solid state. In nature, there are many different types of AC: van der Waals ACs, metallic ACs, fullerenes, molecular, semiconductor, mixed ACs, and their shapes can depart considerably from the common spherical form: arborescent, linear, spirals, etc. Usually, one can distinguish between different types of ACs by the nature of the forces between the atoms, or by the principles of spatial organization within the ACs. ACs can exist in all forms of matter: solid state, liquid, gases and plasmas.

The novelty of AC physics arises mostly from the fact that AC properties explain the transition from single atoms or molecules to the solid state. Modern experimental techniques have made it possible to study this transition. By increasing the AC size, one can observe the emergence of the physical features in the system, such as plasmon excitations, electron conduction band formation, superconductivity and superfluidity, phase transitions, fission and many more. Most of these many-body phenomena exist in solid state but are absent for single atoms. Below we briefly summarize various aspects of AC physics, which to our mind make it an attractive field of research: (i) ACs provide a small, self-contained 'laboratory' in which the major interactions and many-body effects present also in solids can be analysed and studied as a function of their size; (ii) ACs straddle the limit between microscopic and quasi-classical systems, so they can be used to probe the boundary between quantum mechanics and semi-classical systems; (iii) ACs are the appropriate physical objects for studying statistical and thermodynamic laws in nanoscale systems, both classical and quantum; (iv) Small ACs are tractable computationally by *ab initio* methods; (v) ACs can be made and observed in the laboratory by using modern beam or deposition techniques; (vi) ACs provide new examples of many-body forces in a regime which is different from those of atomic, nuclear or solid-state physics, but is related to all of them; (vii) ACs can serve as building blocks for new forms of matter, the formation of AC-based molecules and new materials; (vii) ACs are of similar size to nanoscale devices, and so their physics is closely related to the physics of very small devices, in which quantum effects begin to appear, such as must occur when one wishes to make smaller and smaller chips for microcomputers.

The science of ACs is a highly interdisciplinary field. ACs concern astrophysicists, atomic and molecular physicists, chemists, molecular biologists, solid-state physicists, nuclear physicists, plasma physicists, technologists all of whom see them as a branch of their subjects but AC physics is a new subject in its own right. This becomes clear after a brief study of the problems which atomic AC physics addresses today: (i) The problem of collective excitations in ACs has obvious links in atomic and nuclear physics; (ii) The same is true for the confined atoms problem, and for various collision processes involving ACs; (iii) Fission of charged metal ACs is a process analogous to nuclear fission; (iv) Plasmon excitations, conduction bands, elasticity, superconductivity and superfluidity came to AC physics from solid state physics; (v) Studies of the AC heat capacities and phase transitions have obvious thermodynamic roots; (vi) Studies of AC reactions and AC potential energy surfaces establish links with chemistry and chemical physics; (vii) Studies of electronic and ionic structure and properties of ACs together form a bridge to the molecular biology research of proteins, nuclear acids and other complex biological molecules; (viii) Connections of AC physics to nanotechnology are apparent via quantum dots, quantum wires, nano-tubes and other nano-structures; (ix) ACs are formed in collisions in plasmas and interstellar media. This fact links AC physics to astrophysics, plasma physics and physical kinetics.



▲ **Fig. 1:** Mass spectra measured for *Ar* and *Na* ACs (see [1]. The intense peaks indicate enhanced stability.

Significant progress achieved in the field over the past two decades brought the understanding of ACs as new physical objects with their own distinctive properties. This became clear after such experimental successes as the discovery of the fullerene C_{60}, of the electronic shell structure in metal ACs, the observation of plasmon resonances in metal ACs and fullerenes, the observation of magic numbers for various other types of ACs, the formation of singly and doubly charged negative AC ions and many more. A complete review of this field can be found e.g. in [1].

Distinctive properties of ACs

ACs, as new physical objects, possess some properties, which are distinctive characteristics of these systems. The AC geometry turns out to be an important feature, influencing the AC stability and vice-versa. The determination of the most stable AC forms is not a trivial task and the solution of this problem is different for various types of AC. The stability of ACs and the their transformations is a theme which does not exist at the atomic level and is not of great significance for solid state but is of crucial importance for AC systems. This problem is closely connected to the problem of AC magic numbers.

One can introduce very many different characteristic and properties relevant for ACs, which carry important and specific information about these systems as well as the principles of their organization and formation. In our brief review we are not able even to mention all these characteristics. Thus, we limit ourselves to only a few examples.

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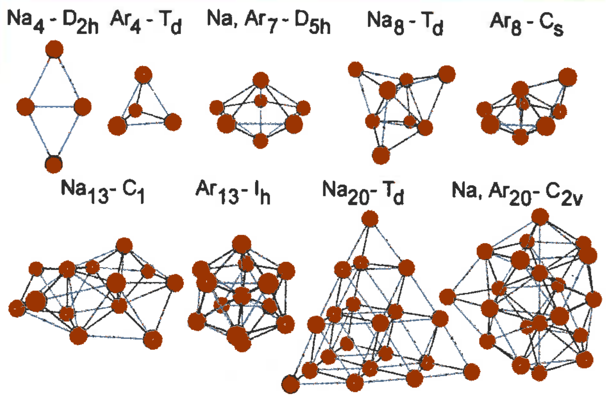
AC magic numbers

The sequence of AC magic numbers carries essential information about ACs electronic and ionic structure [1]. Understanding the magic numbers of an AC is pretty well equivalent to understanding its electronic and ionic structure. A good example of this kind occurs for sodium ACs. In this case, the magic numbers arise from the formation of closed shells of delocalised electrons, one from each atom. Another example is the the discovery of fullerenes, and in particular the C_{60} molecule [2], by means mass spectroscopy.



▲ **Fig. 2:** Geometries and the point symmetry groups of some *Na* and *Ar* ACs calculated in [3,4].

The formation of a sequence of magic numbers is closely connected to mechanisms of AC formation and growth. It is natural to expect that one can explain the magic numbers sequence to find the most stable AC isomers by modelling mechanisms of cluster assembly and growth [3].

In Fig. 1, we present the mass spectra measured for *Ar* and *Na* ACs (see [1]), which clearly demonstrate the emergence of magic numbers. The forces binding atoms in these two different types of ACs are different. The argon (noble gas) ACs are formed by van der Waals forces, while atoms in the sodium (alkali) ACs are bound by the delocalized valence electrons moving in the entire AC volume. The differences in the inter-atomic potentials and pairing forces lead to the significant differences in structure between *Na* and *Ar* ACs, their mass spectra and their magic numbers.

In Fig. 2, we present and compare the geometries of a few small *Na* and *Ar* ACs of the same size. It is clear from Fig. 2 that the principles of AC organization are different for the alkali and noble gas families. Such differences can easily be explained. The van der Waals forces lead to enhanced stability of AC geometries based on the most dense icosahedral packing. The the most prominent peaks in mass spectra of argon ACs correspond to completed icosahedral shells of 13, 55, 147, 309 etc. atoms. The origin of the sodium AC magic numbers is different. In this case the AC magic numbers 8, 20, 34, 40, 58, 92 etc. correspond to the completed shells of the delocalised electrons: $1s^2\ 1p^6\ 1d^{10}\ 2s^2\ 1f^{14}\ 2p^6$ etc.. This feature of small metal ACs make them qualitatively similar to atomic nuclei for which quantum shell effects play the crucial role in determining their properties [5].

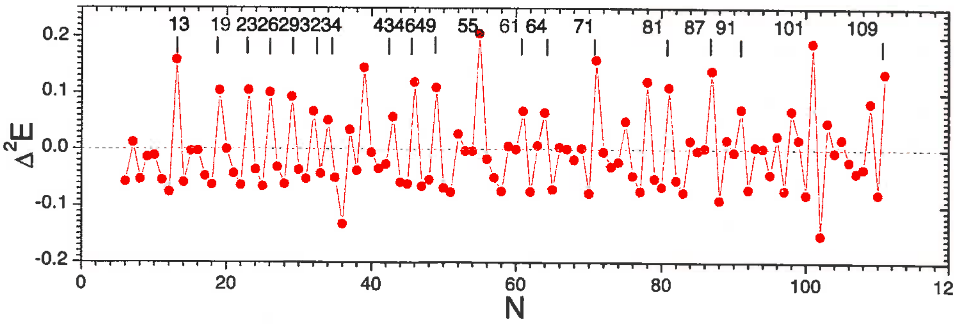
The enhanced stability of AC systems can be characterized by computing the second differences in AC binding energies. In Fig. 3, we present the second differences in *Ar* ACs binding energies calculated in [3]. The correspondence of the peaks in Fig. to those in the *Ar* ACs mass spectrum shown in Fig. 1 is readily established.

Plasmon excitations

Electron excitations in metal AC systems have a profoundly collective nature. They can be pictured as oscillations of electron density against ions, the so-called plasmon oscillations. This name is carried over from solid state physics where a similar phenomenon occurs. Collective electron excitations have also been studied for single atoms and molecules [6]. In this case the effect is known under the name of the shape or the giant resonance. The name giant resonance came to atomic physics from nuclear physics, where the collective oscillations of neutrons against protons have been investigated [5]. The interest of plasmon excitations in small metal ACs is connected with the fact that the plasmon resonances carry a lot of useful information about AC electronic and ionic structure. By observing plasmon excitations in small metal ACs one can study, for example, the transition from the pure classical Mie picture of the plasmon oscillations to its quantum limit or to detect AC deformations by the value of splitting of the plasmon resonance frequencies. The plasmon resonances can be seen in the cross sections of various collision processes: photabsorption and photoionization, electron inelastic scattering, electron attachment, bremstrahlung [1]. Both surface and volume plasmons can be excited. In electron collisions and in the multiphoton absorption regime, plasmons with large angular momenta play an important role in the formation the cross sections of these processes [7].

Fission process

Multicharged ACs become unstable towards fission. The process of multicharged metal ACs fission is qualitatively analogous to nuclear fission. The fission instability of charged liquid droplets was first described by Lord Rayleigh in 1882 [8] within the framework of classical electrodynamics. For review of recent work on metallic AC fission see [1]. The fission process is a complex process in which the evolution of AC shape, AC deformations, many-electron correlation and shell effects play the important role. For more details, we refer here to the recent work [9].



▲ **Fig. 3:** Second differences in binding energies calculated for for *Ar* ACs in [3].

Atoms and ions trapped in ACs: confined atoms

Another problem closely related to AC physics is the *confined atom* (see [10]). This name is given to an atom surrounded by a symmetrical cage of other atoms, and to the modification of its quantum properties which result when it is trapped in this way. The first studies of confined atoms go back nearly as far as the origins of quantum mechanics, and interested such great pioneers as Arnold Sommerfeld, who co-authored a paper on the subject. Recently, there has been a revival, stimulated in part by the observation of the so-called metallofullerenes, in which a metal atom is trapped inside the hollow cage of a C_{60} or larger fullerene. Other forms of confinement also exist. For example, a metallic ion can also be inserted into a noble gas AC, which usually causes a rearrangement, modifying the magic numbers.

Conclusion

In recent years, AC physics has made very significant progress, but a large number of problems in the field are still open. The transition of matter from the atomic to the solid state implies changes of organization which turn out to be a good deal more subtle and complex than was originally supposed. Different type of ACs, composite ACs, various size ranges, AC geometries, complex molecules (including biological), ACs on a surface and in plasmas, all provide additional themes which make this field of science very rich and varied. Collisions involving ACs, mass spectroscopy and laser techniques provide tools for experimental studies of the AC structure and properties. However, what are the experimental limitations? Where should the theory go next? Where does the future lie? Could ACs one day become the smallest devices or be used to make the smallest devices? Could one manipulate AC isomers for the production new materials and nano-structures? What is the difference between a AC and a virus? What are the principles of the matter self-organization, self-assembling and functioning on the nanoscale? We merely mention such intriguing questions in this paper, but we hope that at least some of them will be resolved during the future development of the new science of AC.

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