

1 Introduction

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1.1 What are Clusters?

From the time of *John Dalton*, when the atomic theory became generally accepted, the study of how matter behaves has divided into two streams. One has been reductionist, concentrating on the properties of individual atoms and molecules. In the 1930's, this line led to nuclear physics and then to particle physics. The other stream has emphasized the properties of very, very many atoms or molecules together, so many that the aggregates they make can be treated as infinite. The realm between these limits concerned only a few independent souls until about the late 1970's. Since then, interest has grown almost explosively in the study of what have come to be called clusters.

Clusters are aggregates of atoms or molecules, generally intermediate in size, between individual atoms and aggregates large enough to be called bulk matter. People sometimes argue (but not very seriously) whether three particles are enough to constitute a cluster. And a mole – $6 \cdot 10^{23}$ particles – of anything is far too many particles to be a cluster; that much stuff is certainly bulk matter. Even a hundred billion particles stuck together, far, far fewer than a mole, behave in most ways like bulk matter. Now, when we talk of small clusters, we mean something containing no more than a few hundred or possibly a thousand particles, and a large cluster implies to us something containing thousands of particles. A useful distinction classifies clusters as small, medium-sized or large. Small clusters are those whose properties vary with size and shape so much that no simple, smooth dependence can be given for their dependence on number of component particles. If the cluster's properties are smoothly varying functions of the number of component particles, the cluster is medium-sized or large. If those properties vary smoothly but still reflect the small size of the cluster and the implications of that size, the cluster is medium-sized. If those properties approach those of the corresponding bulk material, the cluster is large. Large clusters typically have dimensions of order a few nanometers, they are spheres with radii between 1 and perhaps 50 nm, or microcrystals with sides of these dimensions. This puts large clusters into the lower reaches of the "nanoscale" materials, and indeed they are.

Aggregates in the small and middle range differ considerably from bulk matter: they differ in at least two important ways. First, a large fraction of their

component particles are on the surface. For example in a cluster of 55 atoms of argon or sodium, at least 32 are in some sense on its surface. But small clusters also differ from bulk matter because the quantum states of bulk matter occur in bands of states so close together that we can disregard the energy gaps between those states. (We cannot, of course, neglect the gaps between the bands, such as that between filled and empty levels in an insulator or semiconductor, the very property that makes the substance an insulator and not a metal-like conductor.) In a molecule or a small cluster, the spacings between the individual levels cannot be neglected. The spacings of the energy levels depend on the size of the object; the gaps between energy states of small clusters are quite like those of small and medium-sized molecules. Even in large clusters and nanoscale materials, the small dimensions of the particles give them some properties strongly characterized by quantum effects, properties whose counterparts seem quite classical in larger systems.

What are clusters, and how do they differ from molecules? If we try, we can find borderline cases that are difficult to classify unambiguously, but before we come to these, let us deal with the large majority of clusters. Molecules are characterized by having definite compositions and, in most cases, definite structures. A cluster of, for example, silicon atoms, may contain 3 or 10 or 100 atoms or any number between or greater. Its properties depend on the number of atoms in the cluster and so does the most stable structure. But note that phrase, "the most stable structure". While one structure may be more stable than any of several others, most clusters may assume any of a number of structures. Figure 1 illustrates this for a very simple cluster, Ar_7 , one comprised of seven argon atoms. At very low temperatures all the clusters of Ar_7 assume the geometry of lowest energy, the pentagonal bipyramid of Fig. 1a. At higher temperatures, some of the clusters would be found in or near that structure but some could exhibit others of the stable structures, or be near one of them.

How near, and how this comes about, will be one of the main topics of this discussion. But to summarize, clusters differ from conventional molecules because of *composition* and *structure*. For the most part, molecules have definite, highly restricted numbers of atoms and specific compositions. Furthermore they almost always have unique structures. Clusters may be composed of any number N of component particles, and, for most kinds of clusters, as the number of particles of the cluster becomes larger, the number of (locally) stable structures available to the cluster grows rapidly. This latter property has its counterpart in the rapid increase, with number of component atoms, in the number of chemical isomers that exist for a specific composition. However we generally identify each of these isomers as a distinct, isolable chemical species. Clusters of a given composition may exhibit a variety of structures but we generally do not distinguish them as different chemical species. There are, however, a number of exceptions to this, and it sometimes is important to distinguish isomers among clusters of the same composition.

Clusters may be homogeneous, that is, composed of only one kind of atom or molecule, or heterogeneous, made of more than one kind of atom or

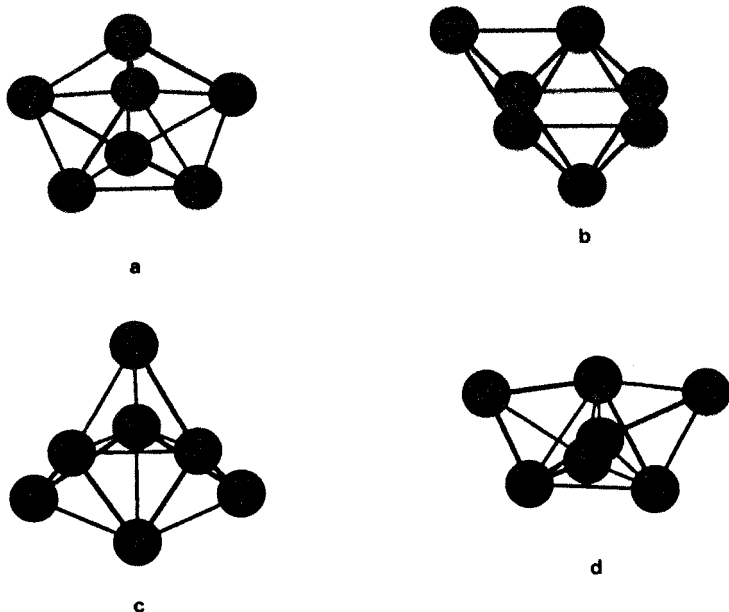


Fig. 1. The four stable forms of the Ar_7 and some other seven-atom clusters. (a) The pentagonal bipyramid, the lowest-energy structure; (b) the next-to-lowest-energy structure, an octahedron with one capped face; (c) the third structure, in order of increasing energy, a tetrahedron with three capped faces; (d) the highest-energy structure of the four, which can be looked at as a bicapped trigonal bipyramid

molecule. Clusters of only silicon atoms or of only argon atoms are homogeneous; a cluster of argon atoms around a molecule of benzene is heterogeneous. So is a cluster of three sodium and two potassium atoms; we could also make a cluster of three sodiums and three potassiums, or two sodiums and three potassiums, and so forth. But this terminology loses its usefulness when we come to clusters of some kinds of molecules, notably salt-like molecules of such substances as sodium chloride. We can make clusters of any number of NaCl molecules which we can designate, in general, as $(\text{NaCl})_n$; an example of this kind of species is shown in Fig. 2. We can also make clusters from NaCl or of other alkali halides with one or more excess alkali atoms or halogen atoms, e.g. $\text{Na}_n\text{Cl}_{n+y}$, or $\text{Na}_{n+y}\text{Cl}_n$. Clusters may be neutral, as in all the examples thus far, or charged: $\text{Na}_{n+1}\text{Cl}_n$ is more likely, under many laboratory conditions, to occur with a positive charge, i.e. as $(\text{Na}_{n+1}\text{Cl}_n)^+$, than as the neutral and the cluster with one excess chlorine atom is often found with a negative charge. These are of course not surprising when we recall that the bulk material sodium chloride is best thought of as composed of positive sodium ions and negative chloride ions. But many other kinds of clusters, neutral and charged, have now been observed and studied.

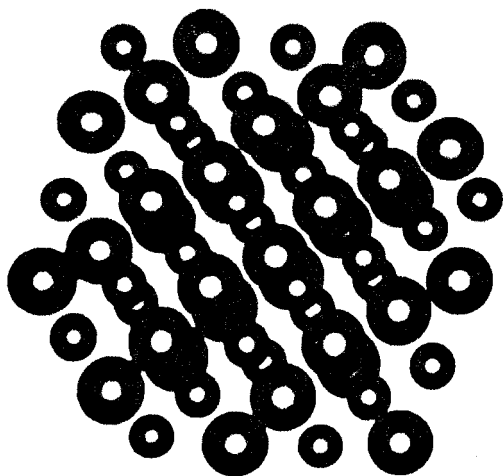


Fig. 2. The $(\text{KCl})_{32}$ cluster in its state of lowest energy. This is the same structure, the rocksalt lattice, as that of bulk KCl crystals

Some clusters are held together by the strong forces of attraction between oppositely charged ions; clusters such as $(\text{NaCl})_n$ are of this kind. Others are held together by the same kinds of strong forces that make covalent chemical bonds; clusters of silicon atoms or of carbon, such as the now-famous C_{60} , are of this kind. Still others are held together by the kind of bonding that holds the atoms of a bulk metal together; we see this kind in the large clusters of metal atoms, large clusters of sodium or copper or iron. Very small clusters of "metal" atoms may be held together by forces more like those of covalent bonds than like the forces exerted by the nearly free-swimming electrons that glue atoms of a metal together. Clusters of the rare gases, and of other closed shell atoms (like very small clusters of beryllium or mercury) belong to the class loosely called van der Waals clusters, held together by the weakest forces that still have their origins in electrical interactions. The last class of clusters we shall single out is that held together by hydrogen bonds. Clusters of water molecules are bound this way; the hydrogens of one water molecule are attracted to specific oxygen atoms of neighboring water molecules. Hydrogen-bonded clusters are held more tightly than van der Waals clusters but less tightly than typical covalent, metallic or ionic clusters.

1.2 What Makes Clusters Interesting?

Clusters have drawn interest for several reasons. Some are matters of technique. We have powerful ways to study clusters, both experimentally and theoretically,

which simply did not exist twenty years ago. Others are reasons of purpose. Clusters may offer ways to make altogether new kinds of materials, to carry out chemical reactions in new ways, and to gain new kinds of understanding, not only of this intermediate form of matter but of the behavior of bulk matter too, by learning how bulk properties emerge from properties of clusters, as the clusters grow larger and larger. In this introductory chapter, we shall examine briefly how people study clusters, and touch on the potential for new materials and new chemical reactions, and how studying the behavior of clusters has been giving us new insights into phase transitions, growth of crystals, chemical catalysis, a new method to grow thin films, high T_c organic superconductors, and above all – the slow transition from atomic/molecular/chemical physics to the science of condensed matter.

1.3 How Does One Make Clusters?

Clusters can be made in the laboratory by making a vapor of the elementary component particles and letting them aggregate, or by knocking them directly out of a solid. They can also, in principle, be made in solution, e.g. as small colloidal particles formed during precipitation or in submerged electric arcs. However most of the work during the explosion of interest in this field since the late 1960's has dealt with gaseous clusters and it is these to which we shall direct our attention. Sources of beams of free clusters are typically one of these: i) the most popular and the best understood source, is the "supersonic jet" with its many variants. A gas or vapor is expanded from a high pressure (typically 10^4 to 10^7 Pa) through a small nozzle (typically 0.03 to 1 mm) into vacuum. The mean gas velocity is increasing during this adiabatic and isenthalpic expansion, but the random, thermal motion of the expanding gas is reduced dramatically. This leads to a reduction of the gas temperature and to effective cluster formation. Some of the popular variants are: a) the source can be run continuous or pulsed, b) a pure gas, say Ar, or a mixture, say He with 1% I_2 , can be used, c) the "mixture" to be expanded can be generated by a powerful pulsed laser or a strong electric discharge, d) the cluster beam can run, after its formation, through a "cloud" of atoms, molecules, electrons, or ions, picking-up some of them, e) an electric discharge can be ignited on the high or low pressure side, f) . . . Many different combinations have been tried and new sources are constantly developed. ii) Another effective means to generate clusters is the "gas aggregation source". Some material is evaporated or sputtered into a slow flow of argon or helium at a pressure of typically 50 to 500 Pa. The atoms are slowed down by collisions with the rare gas, and start aggregating. This process is similar to cloud formation in the atmosphere. In this case water molecules are evaporated. They do not aggregate, if their density is low enough and their temperature is high enough. Only if these conditions are not fulfilled, aggrega-

tion (in common day language cloud formation) starts. Other less common sources are iii) sputtering, or iv) direct laser ablation, without cooling gas.

Once clusters have been made and are in the form of gaseous particles, it is frequently desirable to make them into some kind of controllable beam or stream that can be studied or captured. To observe clusters in a beam, one can probe them while they are free or trap them in a matrix, liquid, glassy or crystalline. Trapped clusters are most easily studied by infrared, visible and ultraviolet spectroscopy. These methods are also used to study free clusters in vacuum. Only for charged clusters has one effective and general means of mass selection and as a result, there are several areas in which more is known about charged clusters than about the neutrals.

One may give clusters positive charge by knocking out one or more electrons, with a beam of electrons or energetic light quanta doing the knock-out. One can also prepare clusters with a negative charge, that is, with an extra electron. These may be prepared by electron transfer from an easily ionized donor such as gaseous rubidium atoms, by capture of electrons from swarms of slow electrons (followed by collision with inert carrier gas atoms or molecules, to carry off the binding energy released by the electron capture and thereby to stabilize the negatively charged clusters), or in the primary process in which the cluster is generated, for example in ablation of material from a solid when it is struck by a high-intensity laser burst or high energy projectile. An effective way to produce intense beams of charged clusters is to generate a plasma in or after the condensation zone. This can be done either by a laser or – less expensively – by an electric discharge.

1.4 Experiments with Clusters

One can eject electrons from neutral or charged clusters. The electrons emitted this way may be collected and studied; so may the newly-produced ions. If one collects electrons, one wants normally to measure their energies. If one collects ions, one may wish to measure their energies and their charge and mass, but Maxwell's laws allows one only to measure the ratio of their charge to their mass.

It is possible to excite clusters, neutral or charged, with light or electron impact and study the radiation they then emit or the particles they lose. The most frequently seen mode for a cluster to lose excess energy is ejection of atoms or larger fragments. It seems that the dominant decay channel is always that having the lowest barrier. If the binding energy of the dimers or trimers is small, atoms are ejected. If the binding energy of the dimer or trimer becomes larger, the ejection of dimers like Na_2 or trimers like C_3 can become the dominant decay channel.

Loss of energy by emission of atoms and of radiation occurs for those clusters which have large band gaps in the bulk, like the rare gases. As there are

no potential curve crossings in the rare gases between the ground and electronically excited states, the electronic energy cannot be converted effectively into heavy particle motion. Thus electronic excitation leads to photoemission. Fission into large fragments is observed only for multiply charged clusters. Loss of an electron can of course occur if the excitation energy is higher than the ionization energy.

Charged clusters have the special attraction that they can be sorted easily by electrostatic, magnetic or time-of-flight mass analysis to yield mass spectra and beams of clusters of a single, known size. The numbers of particles in these beams are very small in terms of macroscopic samples, but are sufficient for many experiments. Among the first studied characteristics of charged clusters were their size distributions, which led to the understanding that some sizes and shapes of clusters are particularly stable, in a manner analogous to the stable shells seen in atoms and in nuclei. The numbers N of particles in these particularly stable clusters are sometimes called "magic numbers". As there is nothing magic about these numbers, some people prefer to use the more appropriate term of "intensity anomalies".

One can study the wavelengths of light that clusters absorb. For some elements – rare gases, alkalis, and mercury – the optical absorption spectrum from the atom and the cluster to the bulk could thus be studied. The first femtosecond experiments on free clusters are just appearing. Some of the other properties of charged clusters that have been studied include their modes of fragmentation, their chemistry, and the effects of their collisions with surfaces.

1.5 Experiments Not Possible Today

Preparing vapours or beams consisting mostly of neutral clusters of only one or a few sizes is still a major unsolved experimental challenge. It can be done only for small clusters with less than 8 atoms if a good supersonic beam of the clusters is available.

A very difficult parameter to control or to determine in all experiments is the temperature of a cluster. Temperature for a finite system may be defined as the mean internal kinetic energy of the heavy particles divided by the number of degrees of freedom. Clusters from neat supersonic beams are hot, boiling hot when they leave the condensation zone. They cool by evaporative cooling, i.e. ejection of atoms or larger fragments. Lower temperatures can be obtained in seeded supersonic beams or in cooled gas aggregation sources. But so far no "thermometer" to measure a cluster's temperature is available. Worse, there does not even exist a suggestion how to construct one. Only if the cluster has enough internal energy to evaporate atoms, metastable decay can be used to monitor the temperature.

Magnetic effects have been studied only for clusters which become ferromagnetic in the bulk. No infrared spectroscopy below $10\ \mu\text{m}$ or radiofrequency

spectroscopy has been performed on clusters. Inner shell excitation of mass selected clusters has not been performed so far. Other unsolved problems are: can a He cluster become superfluid, or can a free Pb cluster become superconductive? How could one detect this experimentally? How could one do, and what could one learn from an $e,2e$ experiment? Looking on the precision and wide range of experiments in atomic, molecular, and solid state science one can say that the science of clusters has made good progress in recent years, but is still very far from being a mature field.

1.6 Clusters, Tantalizing Subjects for Theoretical Studies

Clusters are of course tantalizing subjects for theoretical studies. It is possible to apply to them the same theoretical tools that are applied to studying molecules, the quantum mechanical methods ranging from *ab initio* variational calculations of the entire electronic structure, through more approximate methods such as the local approximations to density functionals which approximate the consequences of electron exchange interactions with effective potentials, to efficient but highly oversimplified, effective potentials to describe the motions of the atoms, molecules or ions comprising the cluster. For clusters of argon, krypton and xenon, Lennard-Jones potentials account for the dynamics nearly as well as more accurate effective potentials; likewise, for alkali halides, Born-Mayer potentials of Coulombic long-range interactions and exponential short-range potentials, represent the dynamics well. For other clusters, more subtle approximations are necessary; for example, embedded-atom potentials are one type of approximate, effective potential that has been used to represent metal clusters. If one can find reliable potentials of the last sort, it is now straightforward to use a computer to solve the simultaneous equations of motion of all the atoms of a cluster, or to explore by statistical sampling the accessible phase space of configurations and momenta of the particles, and thereby carry out computer simulations of the behavior of clusters. Solving the equations of motion is called "Molecular Dynamics" (MD); the statistical sampling methods are called "Monte Carlo" (MC) methods.

Both of these have classical and quantum mechanical forms. Furthermore whenever one has in hand a reasonably efficient representation of the potential, for example a set of pairwise interactions between the component particles, one can carry out various examinations of the surface, such as searches for local minima on the surface or for saddle points, and from these, construct reaction paths for particle motion.

One aspect of the theory of the structure of clusters has brought the subject into close contact with nuclear physics. This is the interpretation of structures of clusters in terms of shell models. This is the idea that clusters of particular sizes have structures that correspond to closed shells of component particles and therefore are relatively more stable than clusters lacking one or a few particles

that would fill out a closed shell, or than clusters with one or a few particles more than the number for a closed shell. The numbers corresponding to completely filled or closed shells are often called magic numbers; examples are 13, 55 and 147 for clusters that take on icosahedral geometries. The shells here refer to shells of atoms. In metallic clusters, particularly the clusters of alkali metal atoms, the determinant of the shell structure is the electron shell structure. A widely used model for these clusters is the Jellium model, which puts the electrons into a continuous, spherical sea of positive background charge. This model has been refined and made self-consistent, and extended to distorted, nonspherical geometries. However it seems that electronic and atomic forces compete for the dominating role in fixing what forces establish the shell structure and stable geometries of clusters. Small, medium and even moderately large alkali metal clusters have structures determined by their electronic shell structure; quite large clusters of alkali metal atoms have structures that are determined by the shells of atoms that can make them up.

Clusters may exhibit different structures under various external conditions of temperature and pressure. They can show many of the characteristics of solid-like and liquid-like behavior and of the equilibrium and passage between these forms. Some clusters can, under the right conditions, behave like soft solids or like slush. Here is one of the areas in which new phenomena have appeared and new insights have arisen concerning the dynamics of small, medium, and large clusters, and into the nature of phase transitions. Clusters may take on a variety of structural forms, some of them identifiable with particular geometric shapes, others with no specific shape but nevertheless characterizable by some degree of floppiness which, in the extreme, is the same as that of a liquid.

1.7 Clusters Make New Kinds of Materials

Clusters offer several ways to make new kinds of materials, all of them still at the frontiers of research. One is based on the differences between the structures of small clusters and the structures of bulk matter. Many kinds of small clusters have for their most stable forms structures based on polyhedra – the cube, the octahedron and especially the 20-faced, 12-vertex icosahedron. One can build an infinite, repeating array of atoms arranged in cubes or octahedra, but not in icosahedra. One can make infinite arrays from icosahedral structures called quasicrystals, but they do not have the regular, repeating structures we associate with crystals. Instead, while they may show order at short distances, they have a degree of randomness at long distances, if the arrays are allowed to grow large enough. However if one can make regular icosahedral clusters of silicon, for example, each containing 13 silicon atoms – one in the center and 12 others on each of the 12 equivalent vertices of the icosahedron, then one can condense these clusters to form a bulk crystal with regular, repeating units, each a 13-atom cluster. Or one could use icosahedral clusters of 55 atoms each, or of 147 or 309

or 561 atoms, or, in principle, the higher numbers that just complete a regular icosahedron. These are called the Mackay icosahedra, after A. Mackay who pointed out their potential importance in 1962. The properties of a crystalline solid built from regular, repeating icosahedral units will surely be different from those of arrays of individual atoms, but in what ways we do not yet know.

A related solid is the form of carbon built from a regular array of the nearly-spherical balls of 60 carbon atoms, buckminsterfullerene, each molecule of which has precisely the shape of a football (called a soccer ball in the US) with an atom at every corner. This material also forms salt-like compounds with alkalis, up to K_3C_{60} for example, which becomes a superconductor at low temperatures. The C_{60} molecule is an array of 12 five-membered rings and 20 six-membered rings that can be thought of as an icosahedron with planes cutting off all the original 12 vertices, leaving pentagonal faces in their place. Other network-shell structures can be made with 12 five-membered rings and other numbers of six-membered rings; some of these, such as C_{70} and C_{76} , are like ellipsoidal balls, not spherical. In fact C_{70} and C_{76} illustrate a point made earlier: both of these exhibit distinct isomers that can be separated and kept, and there is a school that prefers to call these molecules rather than clusters because of their isolability and distinguishability. Others have been reported, with far more carbon atoms, which are long rods with ends that are presumed to be C_{30} caps like half of buckminsterfullerene molecules. These rods may themselves become or be part of new solid materials.

Other possible new kinds of materials would come from embedding micro-clusters of one material in a host of a different but related substances. For example some investigators have been studying how to introduce unique electrical properties into a material this way. A still more dramatic possibility would be the superatom cluster, a cluster whose core is strongly electron-donating and whose outer part or "rind" is strongly electron-attracting. This structure would have a deficiency of electrons in its core and a surfeit in its rind, just as an atom does. However this superatom could have a core of 55 atoms, for example, not of a single atomic nucleus. Its properties would be different from those of any atoms we now know.

1.8 New Chemistry

Still another facet of cluster science treats the chemical reactions that occur on or within clusters. For example hydrogen molecules striking a cluster of nickel atoms may dissociate into hydrogen atoms that become strongly bound to the nickel cluster. Both hydrogen and ammonia molecules react when they strike clusters of iron atoms. These are examples of reactions that have important counterparts in the chemistry of catalysts. But clusters of metal atoms do not react precisely as the corresponding bulk metals do, even if the metal is in finely divided form, such as micron-sized particles. Even clusters of the same size and

composition but different geometric structure may have differing chemical reactivities. Other kinds of reactions of or in clusters that have been studied are such seemingly-simple processes as the recombination of the atoms of a diatomic molecule imbedded in a cluster but dissociated by the absorption of a sufficiently energetic quantum. Other kinds of photochemistry, yielding products different from the reactants, have also been studied in clusters and specific size-dependent effects have been found.

1.9 Outlook

Clusters can be studied by experiment, theory and simulation with the precision and lack of ambiguity we associate with the study of small molecules. Yet we can control the size of the clusters and conditions under which we observe them so that we can extrapolate their properties from those of small clusters through intermediate sizes all the way to bulk matter. This means that clusters have given us a new way to approach the study of matter, a way that allows us to apply the most rigorous, least approximate tools of physics that we have. Cluster science is not only a fascinating field in its own right; it enriches the fields around it and offers tantalizing possibilities for new materials and processes.