2 From clusters to numbers: experimental aspects

The study of clusters requires a proper understanding and management of their production and handling. As for many other physical systems, production conditions strongly limit the level of details accessible in experiments. It is thus of importance to discuss production mechanisms in order to better understand what is measurable and how. It is thus the first aim of this chapter to make a brief presentation of cluster production mechanisms, in terms of cluster sources. On that occasion, we shall address in particular the limitations set by production techniques upon cluster characteristics (size, charge, temperature). Constraints come also from the second step in the experiments, handling of clusters and measurement of observables. The final part of the chapter is devoted to a survey of basic experimental investigations on clusters, both in terms of tools and accessible observables. We shall here illustrate this by several examples from ongoing cluster research.

Cluster production and analysis are intimately linked. Usually, an experimental set up integrates all elements from the source to the collection of data. Such a complete chain of production/measurements/data storage is made possible by the relative compactness of all the elements in the experimental set up. All in all, cluster physics experiments can be performed in modestly sized rooms of a few tens of square meters at most. A schematic picture of a typical experimental set up is shown in Figure 2.1. It demonstrates the case of the widely used supersonic jet source (see Section 2.1.1.1) associated with a mass spectrometer for cluster selection (Section 2.2.1). Let us briefly discuss the various components of this apparatus.

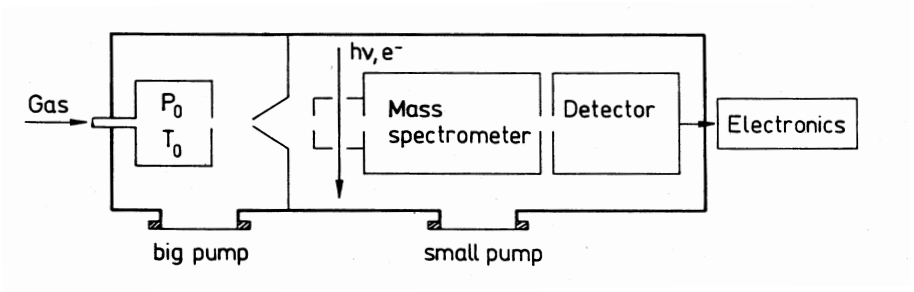

Figure 2.1: Schematic view of an experimental setup. The various components of an experimental apparatus are schematically indicated, starting from the key production device, namely the cluster source. Irradiation by a laser, which produces ionized species, allows mass triggering in a mass spectrometer. Finally, properties of the mass-selected clusters are analyzed in a detector.

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Once produced in the source (left device in Figure 2.1), clusters are ionized either by electron or photon impact. The non-zero net charge thus acquired allows mass selection in the mass spectrometer, an essential step in order to identify the clusters on which experiments are performed. The third compartment in Figure 2.1, labeled "Detector", contains the analysis apparatus itself. As we shall see below, it often employs electromagnetic probing, for example by lasers. The last compartment on the right, sketches electronic devices to store accumulated data. Not shown in the sketch is the very last step of the chain, the data analysis. It is usually done off line. Because this chain is continuous, from production up to data storage, and because it is usually operated as a whole, the production phase is of particular importance as it directly affects experimental outcomes. To a large extent, source managing thus appears as a step in the measurement process. It will be discussed in Section 2.1

As exemplified in Figure 2.1, lasers play a key role in both the handling and the analysis of clusters. We have seen above (in Section 1.2.2) that they are most often driven at sufficiently moderate intensities to remain in a non-destructive regime. Still, this covers a wide range of possibilities and one may wonder what kind of perturbation a laser produces on a cluster. Let us focus on optical lasers, with photon energies of order $\hbar\omega \sim 3$ eV. As we have seen in Chapter 1, such an energy lies close to the range of typical cluster energies. In some cases it may suffice to directly ionize the clusters. The question remains whether the effect is purely energetic or whether such a laser pulse also affects electronic or ionic momenta, and to what extent. Let us consider the example of metal clusters, in which electrons can be viewed as a free Fermi gas characterized by its Fermi momentum $k_{\rm F}$ (see Section 1.3.2). This corresponds to a typical momentum $p_{\rm F} = \hbar k_{\rm F} \sim 0.3 - 0.4\,{\rm eV\,fs\,a_0^{-1}}$, see Table 1.5. It is to be compared to the photon momenta delivered by the laser, $p_{\rm las} = \hbar\omega/c \sim 5 * 10^{-4}\,{\rm eV\,fs\,a_0^{-1}}$. The impact of the laser on the electrons is thus purely energetic and does not contribute to their momenta. The impact on ions is even smaller. Let us estimate typical ionic momenta from ionic vibration energies $E_{vib} \approx 10\,{\rm meV}$. The associated momenta are thus of order $p \sim \sqrt{2ME_{vib}} \sim 4\,{\rm eV\,fs\,a_0^{-1}}$ for Na, i.e. one order of magnitude larger than typical electron momenta and far above photon momenta.

2.1 Production of clusters

Cluster production is a key step in cluster studies. As mentioned above, cluster physics, in particular the study of free clusters, really started in the 1970s with the increasing availability of cluster sources. Without proper and controlled means of production, cluster physics was bound to the study of embedded, or at best deposited, systems. In such cases observed phenomena mix in a complex manner the effects of cluster and substrate or matrix. The start of studies on clusters themselves is thus directly related to progress made at the level of production sources. Not surprisingly, many types of sources have been developed to produce clusters of various sizes and properties. Clusters are finite objects, finite pieces of material. In order to produce them, one can thus either aggregate smaller systems (atoms, molecules, small clusters) or break larger systems (bulk typically). Cluster sources hence basically rely either on condensation/aggregation or on break up, and sometimes on both.

One can thus sort cluster production sources into three main classes. In supersonic jets, a gas is expanded into vacuum from a high pressure through a small nozzle. The subsequent adi-

abatic expansion and cooling leads to cluster formation by condensation. In gas aggregation sources, atoms are injected into a stationary or streaming gas and cluster formation again proceeds via condensation due to cooling of a gas of atoms. In surface sources, on the contrary, clusterization primarily proceeds via break up, in the sense that "proto"-clusters are stripped from a surface by particle or photon impact or by a high electric field, even if some condensation follows. There remains to detail how to activate efficiently these basic production mechanisms. We shall briefly present various types of frequently used cluster sources. One type of source will be discussed in somewhat more detail, namely the supersonic jet sources. This should serve to exemplify the experimental difficulties raised by cluster production, in particular in terms of cluster identification and properties such as size, charge, and temperature. A more detailed discussion of the various sources and their advantages and disadvantages can be found in the review [dH93] or in the books [MI99, Pau00a, Pau00b].

2.1.1 Cluster production in supersonic jets: a telling example

2.1.1.1 Seeded supersonic nozzle sources

The widely used supersonic jets are among the best understood cluster sources. They thus offer an ideal tool to analyze the difficulties encountered in cluster production and identification. The basic idea in such sources is cluster formation by condensation of an expanding gas of atoms [LNH84]. A highly compressed gas (typical total pressure $P \sim 10$ bar) with atoms of the material to be aggregated is allowed to expand through a small nozzle. The ensuing adiabatic expansion slows down the atoms up to a point at which binding between neighboring atoms becomes energetically favorable. This leads to the successive aggregation of the atoms in clusters.

The expansion mechanism is driven by an inert gas carrier. Supersonic sources are often used for producing metal clusters of low melting point metals (usually alkali metals). A furnace contains melted metal which is heated to produce a metal vapor of pressure around 10–100 mbar. This vapor is mixed with (seeded into) a rare gas introduced into the source at a pressure of several bar. The hot mixture of metal vapor and rare gas is driven through the nozzle and expands after the nozzle. This leads to cluster formation as we shall see below. Seeded supersonic nozzle sources are mostly used to produce intense, cold, and "directed" cluster beams with acceptably narrow speed distributions. They allow the formation of clusters with hundreds, even thousands of atoms per cluster with reasonable abundance. A schematic representation of such a supersonic source, together with other "classical sources" is shown in Figure 2.2. One can see on the scheme the basic elements constituting a supersonic source: furnace (left), injection of inert gas carrier (extreme left), heating system (center), nozzle (right) and skimmer (extreme right) ahead of an expansion vessel.

2.1.1.2 Expansion

One starts with an initial gas of atoms at a given temperature T_0. Before atoms are expanded through the nozzle their velocities are random; the high pressure implies a small mean free path (much smaller than the nozzle diameter) and thus a highly collisional regime, which can be typically understood in terms of hydrodynamics. The adiabatic expansion through the

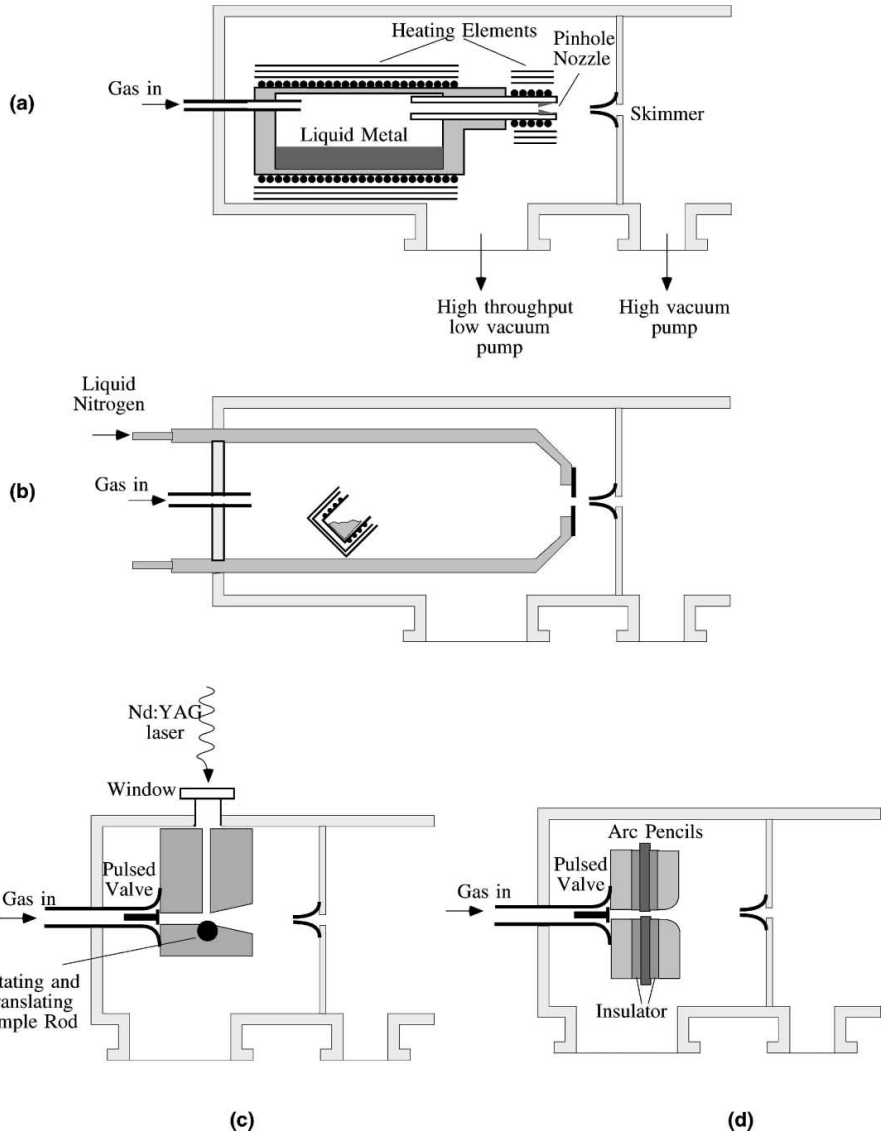

Figure 2.2: Basic layout of typical cluster sources. A seeded supersonic nozzle source is represented in (a), a gas aggregation source in (b) and surface sources in (c) and (d). From [Bin01].

nozzle leads to a strong "alignment" of the atom's velocities (the expansion velocity largely overcomes the original thermal velocity of the atoms). The first phase of the expansion nevertheless maintains an "in flight" hydrodynamical behavior in the system, although with a dramatic reduction of the temperature, pressure and density of the gas. It is during this expansion phase, when a proper "window" of density and temperature is reached, that clusterization

will occur, as we shall see. With proceeding expansion, one reaches a point beyond which the picture of a continuous medium breaks down, and so does the hydrodynamical approach. From then on, each formed particle will more or less follow its own path. The basic properties of the further expanding gas are essentially frozen beyond this instant of "decoupling" of the system. The velocity profile of the expanding gas, for example, turns out to be essentially Maxwellian from then on, with temperature as given by the one at the end of the "hydrodynamical" phase of the expansion.

2.1.1.3 Cluster formation and size distribution

Cluster formation during the expansion proceeds by condensation. It is a complex process which is not yet fully quantitatively understood. The basic condensation mechanism, though, is simple. When atoms in the jet become sufficiently cold, they can bind together to form a dimer (this corresponds to a temperature smaller than the binding energy of the dimer). These dimers (some of them being possibly already present even in the original vapor) constitute seeds for further clusterization. It should be noted here that the kinematics of the expansion process, with only a small spread of atomic velocities, tends to favor this clustering mechanism by keeping atoms in the vicinity of each other. The actual evolution of the system towards the formation of large or small clusters depends on the thermodynamical properties of the jet itself. When the pressure in the jet is small, cluster growth mostly proceeds on the basis of monomer aggregation, basically leading to low mass clusters. A high pressure P in the jet, in turn, allows growth of clusters by cluster aggregation which leads to the production of large clusters. Not surprisingly, the initial pressure P_0 of the gas of atoms is hence directly linked to the actual size distribution of the produced clusters and thus to the abundance spectrum. This feature is illustrated in Figure 2.3 showing mass spectra of CO_2 clusters as obtained under various pressure, and thus clustering, conditions. The initial pressure P_0 is varied between about 0.7 and 3 bar, while the initial temperature T_0 of the atom gas is kept fixed at 225 K. It is interesting to see how the mass distribution strongly depends on P_0. First, note that in all cases one obtains, not surprisingly, a distribution of clusters and not one single species. Both the average value of this size distribution and its width depend on P_0 and both decrease with the pressure. We confirm here the above remark on the fact that low pressure provides a regime of weak clustering (small clusters) while strong clustering can be attained for higher pressures. With increasing pressure P_0 the width of the mass distribution reaches very high values, comparable to the average cluster size. The case at 3000 mbar pressure is quite telling in this respect, with a peak around size 500 and a width (at half maximum) of order 700.

The example displayed in Figure 2.3 exemplifies a basic difficulty in cluster production, namely the fact that one produces a very large variety of clusters in the jet. And it is obvious that clusters with very different sizes will exhibit different physical properties, see the many examples throughout this book. In other words, it is likely that one cannot exploit the cluster beam as is directly formed in a source. A triggering phase is unavoidable in order to select the cluster sizes one aims at studying (see also Figure 2.1). And it is clear as well, that the quality of the production management will directly affect the quality of the measurements. Indeed, if by properly tuning source parameters one can attain an acceptable control on the sizes of the produced clusters, the mass selection will probably become more successful in terms of yield. This allows more accurate measurements on well mass-selected clusters.

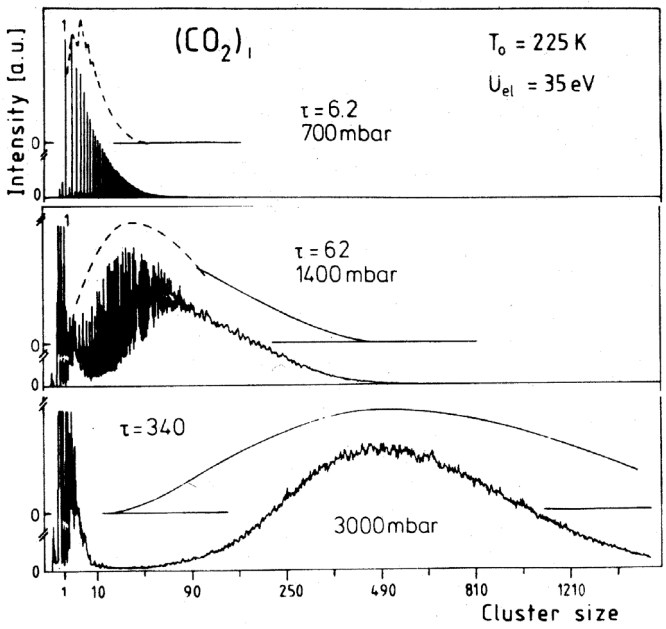

Figure 2.3: Mass spectrum of CO_2 clusters. Under weak clustering conditions, namely at low pressure (upper panel) a roughly exponential mass spectrum is obtained. Higher pressures (going down the panels) leads to better clustering conditions: clusters can then grow by cluster–cluster collisions. This finally leads to a sizeable, although very broad, peak around a finite value of the average cluster size. Full and dashed lines represent theoretical evaluations of mass spectra. After [Hab94].

2.1.1.4 Temperature effects and handling of supersonic jet sources

The poor mass selection of primary clusters (just behind the source) is however not the single difficulty to overcome. The whole production mechanism involves temperature. The expanding gas cools down; its temperature thus depends on the expansion stage. Clustering hence takes place at different temperatures corresponding to different instants of the expansion. Even more delicate is a proper control of the formation heat involved in the clustering process. In other words, clusters are formed at finite temperature. And this temperature results from the decreasing global temperature of the collectively expanding system and from the formation heat in each aggregation mechanism, making it specific to the history of each cluster. The problem looks even more complex when realizing that clusters in the jet may also cool down, for example by collisions inside the jet, or by monomer evaporation (basically due to the fact that clusters have a finite temperature). In order to understand the thermal behavior of the clusters during the aggregation phase, one has thus to account for all these competing processes, for example by employing a statistical model when the temperature is high enough. But all the details of these models, in particular at the level of evaporation rates, are not known, rendering these approaches not fully predictable. The population of clusters formed in the jet will thus exhibit a temperature distribution which is obviously not easy to predict precisely. One might

wonder, though, whether this cluster temperature is likely to affect cluster properties. Roughly speaking, the temperatures attained may be comparable to the clusters dissociation energies, which obviously make them crucial, even for the existence of the clusters themselves. We shall see below that even moderate temperatures may have an important impact (Section 2.1.3.1). All that makes a better control over temperature desirable. This can be achieved by mixing the cluster beam for a while with an inert-gas beam of well defined temperature [ESS+95]. Heat exchange by collisions brings the clusters into thermal equilibrium with the cooler-gas. This allows one to tune temperature over a broad range and in particular to cool down the cluster beam, when necessary.

All in all, this brief overview of cluster production in supersonic jets clearly points out the difficulties one faces in the identification and characterization of formed species. The proper tuning of source parameters thus turns out to be an essential ingredient of any experimental program. As we have seen above, there are no definite models to handle these parameters precisely, although one understands basic underlying physical mechanisms. And of course, experience in the handling of sources becomes essential. In the case of supersonic jets, there thus exist scaling laws for cluster formation involving the initial pressure P_0 and temperature T_0 of the atom gas, as well as the diameter D of the nozzle. For example, it is known that cluster size increases with increasing P_0 or D and decreasing T_0. Usually the distribution of formed clusters is broad. It should also be noted that, in such a condensation process, impurities in the gas play a big role. They may constitute condensation germs and lead to an increase of average cluster sizes.

2.1.2 More cluster sources

There are many types of cluster sources, which actually all have their own merits. In Section 2.1.1, we have seen how clusters can be formed in the widely used supersonic jets. We want here to consider some other types of sources involving various clusterization mechanisms. Again, we skip the details and keep the discussion at a qualitative level, considering only the most common types of sources.

2.1.2.1 Gas aggregation sources

Gas aggregation sources provide a simple and efficient means to produce large clusters. They are, so to say, laboratory copies of a smoking fire or of cloud and fog formation in nature. The basic production mechanism is simple and well known [SMR80]. A liquid or a solid is evaporated into a colder gas which cools down the evaporated atoms or molecules until condensation starts. Condensation then roughly proceeds as in supersonic jets. The dominant clustering mechanism is here successive atom addition. The major difference with supersonic jets lies in the kinematics of the condensation process which is directional in a jet and not so in an aggregation source. As a consequence there is no "automatic" stopping of growth in an aggregation source contrarily to the case of supersonic jets in which the expansion stops clusterization at some stage. All in all, the condensation process is thus more involved in aggregation sources than in supersonic jets. There have, nevertheless, been quite successful applications of aggregation sources. The most famous example of such (so called) smoke sources are the facilities used to produce fullerenes (C_{60}, C_{70},...). But gas aggregation sources have also been used to

produce metal clusters, both with alkalines or more refractory metals [dH93]. The intensities of the cluster beams extracted from the gas aggregation sources are nevertheless much lower than from supersonic jets. A typical layout of a gas aggregation source is shown in panel (b) of Figure 2.2. The cold inert gas injected from the left causes the heated vapor (center) to become supersaturated, which allows cluster production. The cluster beam is then ejected through the right aperture.

2.1.2.2 Surface sources

The principle of surface sources is primarily different from both supersonic jets and aggregation sources in the sense that initial cluster formation mostly results from break up. The idea is to remove finite pieces of material from a solid surface. Nevertheless the ablation phase is usually complemented by a further clustering phase which again proceeds via condensation. The first "erosion" phase can be achieved by heavy particle impact, for example a Xe^+ at a few keV kinetic energy, in the so called Surface Erosion Sources or sputtering sources. By hitting the surface the projectile ejects atoms, molecules or clusters. When the charged projectile is replaced by photons, typically from a laser with intensity $I \gtrsim 10^8$ W cm^{-2} one speaks of a Laser Evaporation Source (LES) [DDPS81]. Extraction can also be achieved by a high-current pulsed arc discharge in the so called Pulse Arc Cluster Ion Source (PACIS) [SLF$^+$91]. The handling of such sources is technically quite demanding. Because the formation process is violent, clusters are usually formed at very high temperature. In order to overcome this temperature problem, such sources have often been coupled to supersonic jets or aggregation sources to cool down the formed clusters. A typical setup, as illustrated in Figure 2.2 (panels (c) and (d)) will thus associate an "ablation" compartment (central part) to a gas carrier injected from the left, as in a gas aggregation or a supersonic jet device. The cluster beam is finally ejected to the right.

2.1.2.3 Pick up sources

Pick up sources are typically used to produce mixed clusters composed of various materials. The idea is to mix clusters as formed in supersonic jets with a jet of other molecules. This allows, for example, attachment of the latter molecules on clusters formed in the jet. Jet mixing can be done at one location (two orthogonal jets) or "in the flight" (two parallel co-expanding jets). Pick up sources are also used to produce relatively cold jets of charged clusters by using a jet of charged particles (electrons, ions).

2.1.2.4 Embedded and deposited clusters

Up to now we have only discussed how to produce free clusters. However the field of embedded and deposited clusters is of great practical importance and it allows several studies which are not easily possible with free clusters. The substrate fixes the clusters and thus gives much more time for growth. This, in turn, allows one to collect much larger clusters when wanted. Moreover, one can achieve a higher density of cluster. The high density of scatterers thus enables measurements with weak signals, as e.g. the second-harmonic generation (SHG), see

e.g. Figure 5.2, or Raman spectroscopy, see e.g. Figure 5.15. Last not least, it is also much easier to control cluster temperature via the substrate.

There are two basically different methods to produce embedded clusters or clusters deposited on a substrate. The first method is growth from supply of atoms or ions. An example of deposited clusters is the growth of Na clusters on an insulating substrate by exposing the substrate to a Na vapor, see e.g. [KWSR99]. An example of embedded clusters is the growth of Ag clusters in glass by diffusion from a surrounding molten Ag salt and $\mathrm{Na}^+ \leftrightarrow \mathrm{Ag}^+$ ion exchange, see e.g. [SKBG00]. The average cluster size can be controlled to some extent by the growth conditions, such as temperature, pressure and time. The method is applicable only if the combination of materials tends to clustering of the vapor atoms or ions respectively. In the case of deposited clusters, a high mobility of the deposited clusters on the surface remains, which may perturb long time measurements by drift and reactions. This can be avoided by sputtering defects onto the substrate before cluster growth, see e.g. [MPT$^+$00].

The alternative method of embedded or deposited cluster production relies on producing free clusters first and depositing them in a second phase onto the substrate or into the matrix. Much depends here on the kinetic energy of the clusters impinging on the material. One distinguishes three regimes [Bin01]: low ($E_{\mathrm{kin}} < 0.1\,\mathrm{eV}$), medium ($0.1\,\mathrm{eV} < E_{\mathrm{kin}} < 10\,\mathrm{eV}$), and high energy impact ($10\,\mathrm{eV} < E_{\mathrm{kin}}$). These produce different results. The low impact deposit places the clusters more or less gently on the substrate. The clusters remain mobile and may rearrange by diffusion along the surface and reactions. The medium impact case pins small defects into the surface which fixes the deposited clusters; however, with the danger of heavily perturbing the clusters themselves. The high impact deposit causes severe damage producing a new composite rather than a deposited cluster.

A problem with embedded or deposited clusters is mass selection. The growth from vapor produces a broad distribution of masses and shapes which can be controlled only roughly through the growth conditions. The explicit deposit of free clusters allows one, in principle, to deal with a beam of mass selected clusters. This holds, however, only before deposit. The actual process of attachment changes the clusters and produces again some spread in masses. There have however come up recently techniques for a size and shape selection of deposited clusters by intense laser fields, see [WBGT99] and Section 5.3.2.

Another problem shows up in connection with the theoretical description of embedded and deposited clusters. The environment has significant impact on the cluster properties. Models for that are yet in a developing stage, see e.g. Section 3.4.4. On the other hand, the many conceivable combinations for cluster and environment generate a huge variety of scenarios whose exploration is an extremely interesting task, see e.g. a demonstration in Figure 5.10. After all, this rich and demanding field is very open for future research. Therefore one will find many further examples for studies with embedded/deposited clusters in Chapter 5.

2.1.3 Which clusters for which physics

The above brief overview of the most commonly used types of cluster sources has shown that cluster production is a delicate but essential step of any experimental program. Clusters are usually formed in ill defined conditions (poorly known size and/or temperature). This calls for the best possible handling of source parameters. After that, one needs a post processing (mass selection mostly), before one can use the beam for measurements. In this section, we will