The physics and technology of cluster beam sources

2.1. Introduction

Large clusters formed in solution, generally referred to as colloids, have been known since the 18th century, and were studied extensively by Faraday (1857). They are important in chemistry because of their high catalytic activity in solution and their use for preparation of highly dispersed supported-metal catalysts. Although it is possible by following highly specific preparation procedures (mostly discovered by trial and error) to produce very narrow size distributions in the solution (*e.g.* Matijevic, 1992; Williams, 1992), this method is mostly unsuitable for application to ultra-high vacuum deposition experiments, or indeed, to the formation of a cluster beam!

Clustering in supersonic molecular beams was discovered much more recently, and in most cases is an unwelcome problem, avoided by warming the source nozzle to prevent the onset of condensation as the beam expands and cools. The opposite technique—cooling the nozzle—has been used to produce beams of van der Waals clusters such as helium, argon and carbon-dioxide, but this technique is not directly applicable to the production of clusters of stronger bonding materials such as metals. (The practical production of metal clusters by the supersonic expansion method is discussed later in section 2.2.1.)

One of the simplest methods of producing metal clusters in relatively large quantities is to evaporate the metal in a bell jar filled to a pressure of a few millibars with an inert gas such as argon or nitrogen. Typically, a black sooty deposit is coated onto the inside of the bell jar. The first recorded experiment of this type was carried out by Pfund in 1930. To form a cluster *beam* from this method presents some considerable extra complications, but this technique is the basis of the inert gas condensation cluster beam source described in section 2.2.2.

This chapter reviews the most common methods of producing a cluster beam in vacuum. The performance criteria for the source described in chapter 3 and used in the experimental work described in chapter 4 are laid out and the reasons given for the choice of the inert gas condensation type of source. Following this, I present a more detailed survey of the processes involved in the inert gas condensation cluster source, including the application of classical nucleation theory and its limitations. Finally, I review briefly some relevant techniques from molecular beam technology and relate them to the problem of extracting a usable cluster beam from the free-jet expansion of the source chamber.

2.2.   Review of cluster sources

Several different techniques for the production of clusters in the laboratory have grown up in line with the differing requirements of various experiments. When designing an experimental system, there are fundamental choices to be made, depending on whether the experiment involves free clusters where a pulsed source may be appropriate, or deposited clusters where the requirements are likely to be a continuous intense beam with a small energy spread. Also, there is the type of cluster required—the size and species, whether the clusters should be ionised, what temperature they should have, and so on. Here, I review six of the most commonly used sources for producing metal cluster beams, illustrated schematically in figure 2.1.

2.2.1.   Supersonic expansion

This technique exploits the adiabatic cooling of a stream of gas when it expands into a vacuum from a small nozzle. In this isentropic expansion, the density and translational temperature decrease with distance from the nozzle (Miller, 1988), and clusters form if sufficient collisions occur before the beam becomes too rarefied and cooling stops. In the case of metals, expansion of pure metal vapour from an oven produces clusters of only a few atoms. For this reason, seeded supersonic nozzle sources are generally used, in which an inert gas such as argon at a stagnation pressure of several atmospheres is mixed with the metal vapour, which is heated to produce a partial pressure in the range 10–100 mbar. The inert gas cools rapidly on expansion, and this helps to cool the metal vapour through collisions.

The seeded supersonic expansion method is only suited to low-boiling point metals because of the practical difficulty of heating the entire source to a sufficiently high temperature to vaporise the metal. The clusters in the beam tend to contain up to a few hundred atoms, and have a low translational temperature (thus a narrow speed distribution in the beam) but a high vibrational temperature, which may lead to evaporation of atoms from the cluster in flight. The geometry of the nozzle is important. Constraining the expansion of the beam by use of a conical nozzle favours cluster production by increasing the number of collisions in the beam. This also increases the centre-line flux and leads to larger clusters. The first successful seeded supersonic expansion source was constructed by Kappes *et al.* (1982). Under special conditions, clusters of up to several thousand atoms may be formed (Pedersen 1991).

2.2.2.   Inert gas condensation

In this technique, the metal is evaporated into a flowing stream of cold inert gas, which cools the vapour so that it becomes supersaturated and condenses into clusters. The clusters entrained in the inert gas flow out through a nozzle into the high vacuum region. Superficially, it is similar to the supersonic expansion method, but the clusters are formed *before* the expansion into the high vacuum region. The cooling effect of the inert bath leads to clusters with a low internal temperature (de Heer 1993) so that re-evaporation is usually negligible, although there is some disagreement over this in the literature
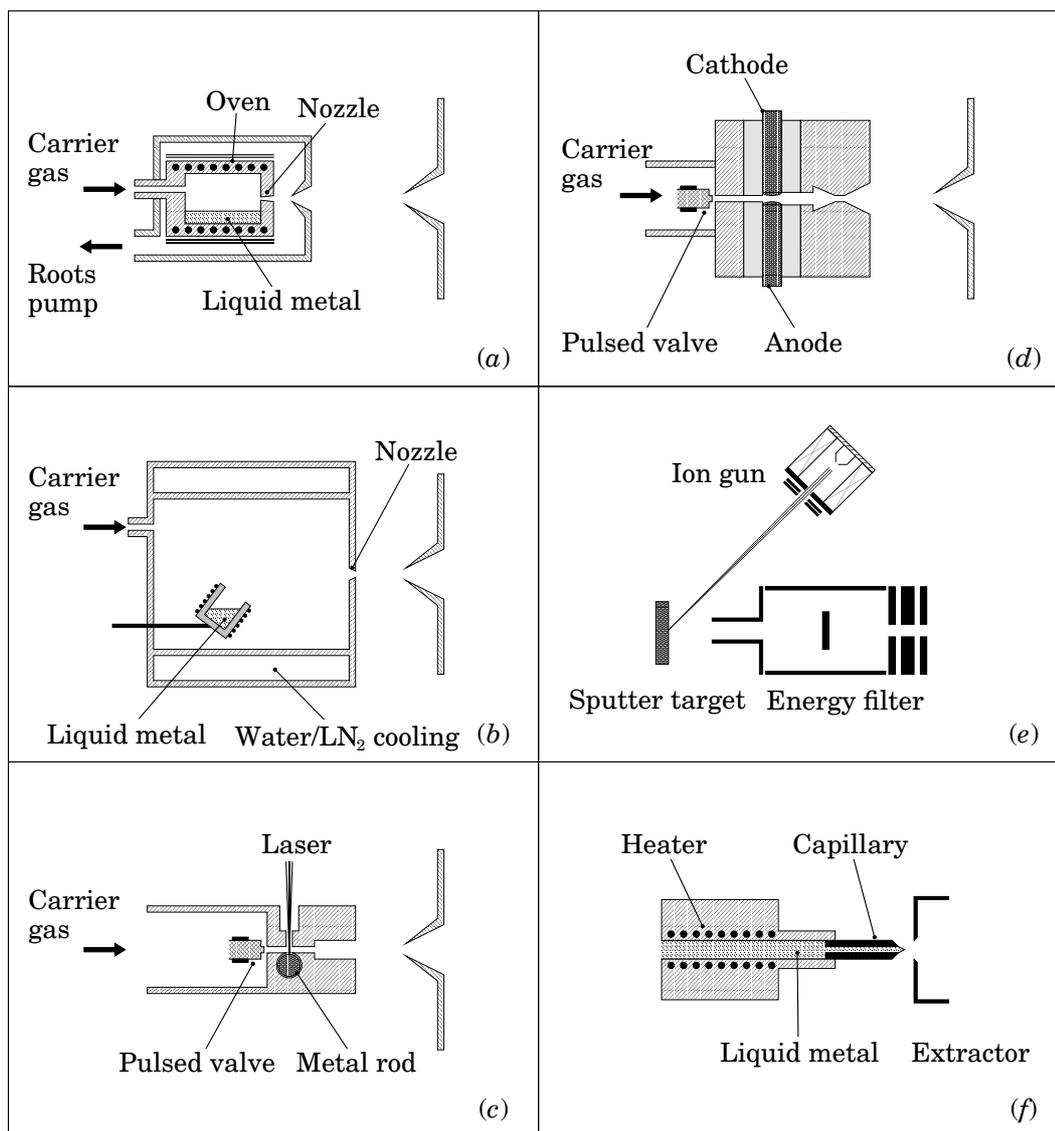
Figure 2.1 (*a*) Seeded supersonic nozzle source, (*b*) gas condensation source, (*c*) laser vaporisation source, (*d*) Pulsed Arc Cluster Ion Source, (*e*) Sputter source, (*f*) Liquid Metal Ion Source.

(Kappes 1988). Because the supersonic expansion is weak, the larger clusters tend not to be accelerated to the same velocity as the carrier gas so that the kinetic energy spread in the beam is generally well below 1 eV. Evaporation temperatures higher than those attainable in the supersonic expansion source are possible, since only the crucible is heated, so that clusters of silver, nickel, iron, and so on may be produced.

Clusters produced by inert gas condensation range in size from dimers to ~10^5 atoms, controlled by the growth conditions. Abundances tend not to reflect the relative stabilities of the clusters. The prototype source by Sattler *et al.* (1980) produced clusters of antimony, bismuth, and lead containing up to a few hundred atoms, but with a detected count rate of around ten per second. Needless to say things have improved significantly since then so that cluster ion intensities of around 10^{10}–10^{11} per second are achievable.

2.2.3.   Laser vaporisation

The laser vaporisation source is a pulsed source that is able to produce clusters of almost any metal, including refractory metals. Metal vapour is generated by the pulsed-laser ablation of a target. A pulsed flow of cold inert gas entrains the vapour, as in the inert gas condensation source, and the geometry of the growth channel strongly influences the size of clusters produced (Heath 1985). Because much higher stagnation pressures are used than in the inert gas condensation source, there is a further significant cooling on expansion into the high vacuum region. The clusters produced tend to contain up to a few hundred atoms.

2.2.4.   Electrical arc discharge

The electrical arc discharge source or PACIS (Pulsed Arc Cluster Ion Source; Siekmann, 1991) is based on the laser vaporisation source, but an electrical arc is used to vaporise the material directly, rather than indirectly through a laser pulse. For this reason, about ten per cent of the clusters formed are ions, which avoids the need for a separate cluster ionisation stage. Cluster sizes are up to around fifty atoms, and the intensities are very high—up to a few ångstroms deposited on a target per pulse in some cases.

2.2.5.   Ion bombardment

Ion bombardment, or sputtering, involves bombarding a target of the cluster material with heavy high-energy ions, which effectively 'chip off' clusters of atoms. Given a powerful enough ion gun, it is possible to obtain reasonably large cluster fluxes from the source. But the technique is only really suited to producing clusters of small size, since the intensity distribution tails off exponentially with cluster size. Despite this, Fayet *et al.* (1992) produced platinum clusters of up to 10 atoms using a 30 keV xenon ion gun. The exact mechanism by which clusters are sputtered from the target remains unclear but it is known that the clusters produced are hot and cool down by evaporation in flight. Clusters of positive and negative charge are produced, as well as neutral clusters. One problem with this source is in the difficulty of soft-landing ions on a substrate, due to the large energy spread of the sputtered ions, typically up to 30 eV.

2.2.6.   Liquid metal ion source

To produce multiply charged clusters of low melting point metals, a liquid metal ion source (LMIS) may be used. It consists of a capillary filled with the liquid metal, to which a large electric field is applied. The electric field pulls the liquid metal at the entrance to the tube into a Taylor cone (Taylor, 1965). At the tip of the cone, the field is so intense that cluster ions may be torn off. These clusters are hot, and cool in flight by evaporation. Coulomb explosion may also occur as multiply charged clusters are common. DiCenzo *et al.* (1988) used this method to produce gold clusters of up to thirty atoms. Unfortunately, this source suffers from the same large kinetic energy spread in the beam as the sputtering source.

2.3.   Performance criteria for a cluster deposition source

The chief aim of the project was to deposit small to medium sized clusters of silver or other similar metals onto a substrate under ultra-high vacuum conditions, such that the clusters on the substrate would have a well-defined size. This immediately raises a number of criteria for the performance of the source.

- The source should be able to produce clusters of the desired size range, *i.e.* of around 2 to 200 atoms.
- The clusters should be ionised to enable mass selection, focusing, and so on.
- A mass filter should be included so as to select the desired cluster size. Ideally, it should be possible to select a single size at the smaller end of the scale, while at higher masses a narrow distribution of sizes would be acceptable.
- The source should be able to produce clusters of silver and other similar metals.
- It should be possible to land the clusters on the substrate in a controlled manner so that they do not break up under the force of impact.
- The attainable beam intensity should be sufficiently high that experimental time-scales are practical.
- An additional criterion is that of reasonable cost.

2.4.   The choice of source type

Figure 2.2 presents a summary of the relative performance of the different types of cluster source discussed above, as given in the literature. The final choice of cluster source is that which satisfies as many of the criteria given above as possible.

2.4.1.   Cluster size

The sputter source and the LMIS both produce small clusters with a size distribution that tails off rapidly with increasing size. The supersonic expansion source, the PACIS, and the laser vaporisation source generally produce clusters of up to a few hundred atoms. The gas condensation source can produce clusters of considerable size and offers great flexibility in the size range.

2.4.2.   Ionisation

Ionisation of a neutral beam is usually (though not always—see section 3.6) an inefficient process, so a source that produces ions rather than neutrals may be an advantage. The electrical arc discharge source, the sputter source and the LMIS all produce ions.

2.4.3.   Mass selection

The main requirement placed on the source by the need for mass selection is that it should be possible to produce an ionised beam from the clusters emerging from the source (if they are not already ionised) with a small energy spread. The reason for this is that the magnetic and time of flight types of mass filter are dispersive over energy as well as mass and so demand a small energy spread if good mass resolution is to be achieved. The

	Cluster size / atoms	Beam energy spread	Cluster internal temperature	Cluster material	Charge state of clusters	Beam intensity	Cost
Supersonic expansion	$< 100^a$	small; varies with size^b	hot^a	alkali metals^a	neutrals	very high^a	fair
Inert gas condensation	2 to $> 10^{5\ c}$	small, < 0.1 eV	cold^a	melting points up to silver/iron?	neutrals	high 0.6– 40 nA^d	fair
Laser vaporisation	$< 200^a$	small	cold^a	any metal	neutrals		high
Electrical arc discharge	$< 50^e$	small^e	cold	any metal?	neutrals and ions	v. high: 2 Å per pulse^e	fair
Ion bombardment	$< 10\text{–}20^f$	20–30 eV^f	hot^a	any metal	neutrals and ions	10 nA^f	high
Liquid metal ion source	$< 100^g$	10–50 eV^g 100–200 eV^h	hot	melting points up to gold	ions	20 nA at 2 m^g	fair

Figure 2.2   Comparison of six common cluster source types. The parameters listed are often 'best case' ones, and will depend also on the cluster species and the type of experiment. (*a*) de Heer (1993), (*b*) Miller (1988), (*c*) *e.g.* Abe (1980), (*d*) McHugh (1989), (*e*) Siekmann (1991), (*f*) Begemann (1986), (*g*) Bhaskar (1990), (*h*) Berry (1986).

exception to this rule is if a quadrupole mass analyser is used. A quadrupole is not energy dispersive, but there is a maximum velocity with which the ions can pass through for mass selection to be effective. Also, quadrupoles generally have a rather limited mass range. We will return to this subject in section 3.7.

The LMIS and the sputter source both produce ions, but unfortunately the ions tend to have a large energy spread. The PACIS produces ions with an acceptably small energy spread. The energy spread of ions produced from a neutral beam depends on the design of the ion source, and can generally be made sufficiently small if the range of kinetic energies of the neutrals is not too large. A potential problem with the supersonic expansion source is that the neutral clusters are produced with a particular *velocity*, rather than energy (section 2.7.5), which introduces a systematic variation of energy with mass into the beam. It is possible to correct for this in the calibration of the mass filter.

Another point worth noting in relation to mass selection is that some of the sources—the sputter source, the LMIS and the supersonic expansion source—produce clusters that are apt to fragment in flight (which may happen after mass-selection) due to evaporative cooling or Coulomb explosion in the case of multiply charged clusters from the LMIS. This

objection is tempered slightly by the fact that ionisation of a neutral cluster, even if it is cold initially, can impart enough energy to make subsequent evaporation a possibility—hence the inert gas condensation source, the PACIS, and the laser vaporisation source may present this problem too.

2.4.4.   Cluster species

A fundamental consideration in the choice of source is the material from which the clusters are to be made. The sputter source is able to make clusters of virtually any electrically conducting material; the laser vaporisation source can form clusters of almost anything that can be vaporised by the laser. The seeded supersonic expansion source is best suited to low melting point metals such as the alkalis because of the difficulty of heating the entire source to temperatures much over 1000 °C. The inert gas condensation source, which uses a crucible to evaporate the material, and the LMIS with its liquid metal filled capillary are able to go to higher melting points, around 2000 °C, which although insufficient for refractory metals is adequate for metals such as silver and gold.

2.4.5.   Controlled deposition

The requirement for controlled landing is the same as for mass selection, *i.e.* that the beam must have a small kinetic energy spread. This is to ensure that the clusters have a well-defined low energy as they hit the substrate.

2.4.6.   Source intensity

The cluster flux from the source determines the length of time needed to deposit the desired density of clusters on the surface. If the flux is very small, it becomes difficult to monitor the deposition rate, and the length of time for deposition of a useful cluster density on the surface can become prohibitive. A further consideration is that of contamination of the surface during deposition. The experiments described in this thesis were all done in high vacuum, but it was intended that the source would be useful for ultra-high vacuum experiments also, where a higher standard of cleanliness is normal. In order to gain an idea of the necessary beam flux, it is useful to compare the flux of the beam on the sample with that of the residual gas in the chamber. The flux per unit area of residual gas molecules impinging on a surface is given by

$$\Phi = \frac{P}{\sqrt{2\pi mkT}} \tag{2.1}$$

which at a pressure of 10^{-10} mbar amounts to about 10^{11} molecules per second on a sample of area 1 cm^2. At non-cryogenic temperatures, most of these will not stick, but even the best beam intensities of mass selected clusters tend not to be more than around 10^{10}–10^{11} clusters per second and it is common to end up with a lower density of clusters in the beam than of residual gas molecules in the vacuum!

On a time-averaged basis, the laser vaporisation source produces an inferior output to the others. Whilst the LMIS and sputter source can produce extremely high fluxes of very

small clusters, the flux drops rapidly with increasing cluster size. The supersonic expansion source can produce extremely high fluxes up to a few hundred atoms. Good fluxes have also been achieved with the gas condensation source and the PACIS.

2.4.7.   Operational characteristics

The practical operational characteristics of a particular source may influence the choice. The two main problems with the supersonic expansion source are the high temperature needed for the oven, which makes maintaining a clean vacuum difficult, and clogging of the nozzle or skimmer. The gas condensation source suffers from similar cleanliness problems, and ensuring repeatability and stability of operating conditions can also be a problem, as cluster generation is very sensitive to source conditions. The pulsed type sources generally suffer from pulse to pulse variations in the beam, making optimisation of the beam optics impossible for the entire beam. The sputter source tends to produce a very stable ion beam, which varies little with time. It is an inherently clean method of producing clusters, as there is no requirement to heat an oven up to high temperature. However, due to the low beam energies typically used for quadrupole mass selection, and the very high current from monomers in the beam, space-charge limitations can be a problem. The LMIS is a very clean source producing a stable beam, but the high voltages used can cause arcing.

2.4.8.   Cost

The laser vaporisation source and the sputter source are both rather expensive due to the high cost of a powerful laser or ion gun. The other sources are quite comparable on the basis of cost.

2.4.9.   Final choice

On balance, an inert gas condensation source seemed to give the most flexibility for the experiments proposed whilst meeting most of the requirements. The results of Yokozeki *et al.* (1978), who achieved a flux of order 10^{16} clusters per second—albeit large clusters that were not ionised and not mass selected—and those of others, indicate that it should be possible to produce quite high beam intensities. Some of the advantages of a gas condensation source are that:

- it is possible to control the size distribution of the clusters over a large range by altering parameters such as temperature and pressure, making this source the most flexible in terms of the range of cluster sizes that can be made.
- the clusters are produced with a thermal energy distribution, (*i.e.* a small kinetic energy spread) hence soft landing on the substrate should not be problematical. This also opens up the possibility of using a velocity filter instead of a quadrupole mass analyser to mass select the beam.
- the clusters are cold due to the inert gas bath and so evaporation in flight is unlikely to occur.

- a gas condensation source could be modified to work on the principle of seeded supersonic expansion since from the skimmer region onwards, both sources are essentially identical.

Disadvantages are that:

- a large flow of an inert gas is necessary, involving substantial pumping of the system if the substrate chamber is to be kept under high vacuum during deposition. In fact, the pumps make up most of the cost and bulk of the apparatus.

- it may be difficult to adjust conditions to obtain high fluxes for very small clusters of just a few atoms, although this has been done (*e.g.* Hall, 1991).

- it is not possible (in any simple way at least) to produce clusters of very high melting point elements such as tungsten.

- the clusters are produced as neutrals and so require ionisation which is usually an inefficient process.

- maintaining a clean vacuum may be difficult.

2.5.   A brief history of the inert gas condensation source

Clustering by direct evaporation of a metal into a bath of cool gas was first investigated by Pfund in 1930. He observed the formation of a 'smoke' when bismuth was evaporated into air at 0.25 Torr and room temperature. An intensely black film consisting of very fine particles was deposited inside the chamber, which he used as an absorber of infra-red radiation for thermopiles and bolometers. The next important step was taken by Beeck and co-workers in 1941. They evaporated nickel into an inert nitrogen atmosphere as part of a study into catalysis. They found that the films thus produced were porous and had a much higher catalytic activity than those deposited in high vacuum—even more than could be accounted for by the additional surface area, pointing to a radical difference in properties to those of the bulk.

The experiments of Mann *et al.* (1973) marked an important new direction in cluster physics. They investigated light-scattering by alkali metal clusters as a function of mean cluster size in a flowing stream of inert gas, and related their results to Mie theory in the Rayleigh scattering limit where the particle size is much smaller than the radiation wavelength. This was probably the first true flowing gas condensation source.

One of the goals of cluster research was the production of a beam of size selected clusters so that the averaging over a range of sizes in previous experiments could be eliminated. This was achieved by Sattler *et al.* (1980) by uniting the flowing gas condensation source with a time of flight mass spectrometer. They were able to make clusters of up to a few hundred atoms of antimony, bismuth and lead, although the beam intensities that they detected in the time of flight spectrometer were very low by today's standards—around ten clusters per second.

The basic operational principles of gas condensation sources have not changed significantly since then, but major improvements have been made to the flux and cluster size ranges obtainable by optimising the geometry of both the condensation cell and the

beam extraction—using techniques borrowed from molecular beam technology for example.

2.6.   Cluster nucleation and growth

The formation of clusters within the condensation cell depends upon several complex processes and it has not proved possible so far to formulate a fully quantitative model. Problems include complex gas flow behaviour, the sensitivity to the particular geometry of the cell, and so on. A result of this is that no two gas condensation sources are quite alike, and each must be carefully characterised by experiment. Of various simplified models, classical nucleation theory has been used extensively in order to gain insight into the necessary conditions for nucleation of clusters (Yokozeki 1978, Hall 1991) and also to model nucleation in supersonic expansions (Stein, 1983).

2.6.1.   Classical nucleation theory

Within classical nucleation theory, the nucleus is considered as a sphere of radius r and atomic volume v_L. There is a free energy advantage associated with the formation of liquid from the vapour, which scales with the volume of the droplet, and a free energy cost associated with the surface tension Γ on the droplet, which scales with surface area. The total free energy may be written as:

$$\Delta G = 4\pi r^2 \Gamma - \frac{4\pi r^3}{3v_L} kT \ln S \qquad (2.2)$$

where S is the supersaturation, the ratio of the actual vapour pressure to the equilibrium vapour pressure at temperature T, and k is the Boltzmann constant. This free energy has a maximum for the critical radius

$$r_c = \frac{2\Gamma v_L}{kT \ln S} \qquad (2.3)$$

and has a value given by

$$\Delta G_c = \tfrac{4}{3}\pi r_c^2 \Gamma \qquad (2.4)$$

Smaller droplets are unstable and reduce their free energy by evaporating, and larger droplets reduce their free energy by growing. Equation (2.3) indicates that materials with a high surface tension, such as metals, have larger critical radii than those with lower surface tension at a given temperature. The critical droplet becomes smaller as the temperature or supersaturation in the condensation cell increases. Equation (2.4) shows that the energy barrier to nucleation is highly sensitive to the surface tension and the temperature and supersaturation of the vapour.

The rate of nucleation for droplets greater than the critical size is given by Waldram (1985) as

$$R = \left[v \left(\frac{\alpha}{2\pi} \right)^{1/2} \right] \left[V \left(\frac{n_c mkT}{2\pi\hbar^2} \right)^{3/2} \right] e^{-\Delta G_c / kT} \qquad (2.5)$$
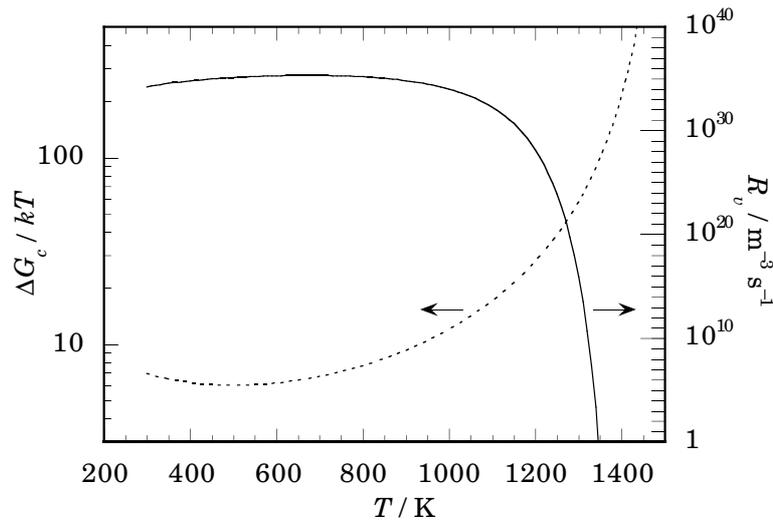
Figure 2.3 Logarithmic plot of the energy barrier to nucleation ($\Delta G_c/kT$ —broken line) and the nucleation rate (R_v —solid line) for silver as a function of temperature at fixed vapour concentration.

where v is the mean rate of arrival of vapour molecules, n_c is the number of constituent molecules or atoms in the critical droplet, V is the volume in which the vapour is contained and m is the mass of each molecule or atom. α is a factor related to the half width of the energy barrier and is given by $2\Delta G_c/3kTn_c^2$. The first term represents an effective attempt frequency for droplets passing through the critical size. The second term is a phase space factor and the third the usual Boltzmann factor. Using this formula and equation (2.1) to estimate v, the rate of nucleation can be found for conditions in the condensation cell. Figure 2.3 is a logarithmic plot showing how the energy barrier and nucleation rate per unit volume, R_v, vary for silver as a function of temperature. The vapour pressure is assumed to be that of the metal at the evaporation temperature of 1500 K. (In practise, the vapour pressure will fall further from the crucible.) The figure shows that nucleation begins suddenly once the vapour has cooled to about 1350 K at which point the supersaturation is about 10 and the energy barrier about 100 kT. The critical radius is about 1 nm, which corresponds to a cluster of around 100 atoms. (It does not matter much what criterion we take for the onset of nucleation, since the rate changes by a factor of about 10^{17} over a temperature variation of only 50 K, but a rate of around 10^{10}–10^{16} m^{-3}s^{-1} is reasonable for an inert gas condensation cluster source.) As the temperature decreases further, nucleation becomes explosively fast, and will in practice be limited by the supply of vapour diffusing from the crucible to the nucleation region just above.

Increase of	Average size	Cluster mass flow rate
crucible temperature	increases[a,c]	increases[c]
inert gas pressure	increases[a,b,c]	increases[c]
inert gas temperature	decreases[b]	
inert gas molecular weight	increases[a]	
inert gas flow rate	decreases[c]	
growth distance	increases[b,c]	increases[b], decreases[c]

Figure 2.4   Dependence of average cluster size and cluster mass flow rate on source conditions. (*a*) Yokozeki (1978), (*b*) Schaber (1985), (*c*) Frank (1985).

2.6.2.   Qualitative predictions of classical nucleation theory

We can use the general principles outlined above to help understand how the behaviour of an inert gas condensation source varies with source conditions. Figure 2.4 summarises some typical experimental results.

2.6.2.1.   *Crucible temperature.* An increase in crucible temperature increases the evaporation rate producing a greater metal flux—hence a greater mass flow rate. The increase in flux from the crucible increases the metal vapour density around the crucible. There is a competition between nucleation of super-critical sized clusters and further growth of these clusters, but the increase in vapour density results in a decrease in the cooling efficiency of the inert gas. So growth tends to win over nucleation and large clusters result.

2.6.2.2.   *Inert gas pressure.* An increase in the inert gas pressure slows the diffusion of metal vapour away from the crucible so that the vapour is enriched. As in the previous case, growth wins over nucleation and larger clusters form. If the inert gas pressure is reduced, vapour diffuses away from the crucible faster and the nucleation zone becomes more spread out. The lack of vapour prevents clusters from growing very large. The increase of mass flow rate with inert gas pressure is due to the efficiency of the inert gas in entraining the clusters—removing them from the crucible region and transporting them out of the condensation cell. At low pressure, many clusters may be deposited on the walls of the condensation cell, but at higher pressure, they are swept along in viscous flow with the inert gas.

2.6.2.3.   *Inert gas temperature.* As the gas temperature is raised, the temperature gradient near to the crucible decreases, and the nucleation zone moves away from the crucible to a region of lower vapour density, resulting in smaller clusters. When the inert gas is very cold, the temperature profile is steepest very close to the crucible so that most of the clusters are nucleated in a region of high vapour density, leading to rapid growth and large ultimate sizes. However, since nucleation does not appear to require a

particularly large drop in temperature (figure 2.3) one would not expect the temperature of the inert gas to have a particularly dramatic effect.

2.6.2.4.   *Inert gas molecular weight.* Increasing the molecular weight of the inert gas increases its cross-section and slows diffusion of the vapour away from the crucible. This is similar to increasing the inert gas pressure.

2.6.2.5.   *Inert gas flow rate.* Increasing the inert gas flow rate reduces the length of time that the clusters spend in the growth region of high vapour density. They have less time to grow and so are smaller. It also increases the effectiveness of the cooling, so that the temperature gradient is larger near to the crucible and more clusters are nucleated. This parameter, coupled with growth distance, probably has the most dramatic effect on the mean size of the clusters.

2.6.2.6.   *Growth distance.* Increasing the growth distance, which in most sources is the distance from the crucible to the exit of the condensation cell, increases the time available for clusters to grow and results in larger clusters. (If the condensation cell is large, then growth may stop when the vapour is exhausted, before the exit is reached.) The effect on the mass flow rate is more complicated and depends primarily on the geometry of the source. Schaber (1985) has suggested that the increase in mass flow rate with nucleation distance in his source is due to the increased volume in which the clusters may be 'focused' by the inert gas onto the condensation cell exit, so less are lost onto the cell walls. In the case of Frank (1985), the decrease in mass flow rate may be due to a decrease in inert gas flow.

In practise, inert gas temperatures from 77 K up to room temperature are used, room temperature being adequate for the formation of small to medium clusters. Inert gas pressures range from 10^{-2} mbar to tens of millibars. The pressure has more effect on the cluster size than the temperature. Depending upon the geometry of the source, production of small clusters at low pressures may be limited by the problem of extracting them from the condensation cell, since at low pressure they are easily deposited on the walls rather than being swept along with the inert gas. An arrangement in which the crucible is tilted to face the exit aperture has been found to help considerably in this respect (Schaber, 1985). It is likely that the relatively high minimum pressure necessary for cluster production to be observed which was reported by some groups has more to do with the fact that at lower pressures the clusters are deposited on the walls of the chamber than that nucleation is actually inhibited.

2.6.3.   Limitations of classical nucleation theory

Despite the success of classical nucleation theory, there are still questions over its applicability to clusters of only a few atoms. It is questionable whether the bulk value of surface tension is the correct value to use for small clusters, or indeed whether surface

tension is really an appropriate way of modelling the unfavourability of surface sites on an atomic scale. However, it is possible to use an 'effective surface tension'. Another problem concerns clusters smaller than the critical size, which according to the theory should not be stable and should evaporate spontaneously. For the silver clusters considered earlier, the critical size in the nucleation zone is around 100 atoms, yet beams containing much smaller clusters than this are routinely generated by this technique. The solution is probably that classical nucleation theory does not allow for temperature changes in the system. A small cluster leaves the growth region before it reaches the critical size but does not evaporate if it contains insufficient internal energy to do so. In the inert gas condensation method, the cooling by the inert gas removes much of the initial thermal energy of the vapour. Other problems pointed out by Kappes (1988) are that the theory ignores rotational degrees of freedom (which effect the value of ΔG_c) and that most real systems have time varying properties that cannot be accommodated easily into classical nucleation theory (although it should be noted that the theory presented by Waldram concerns a dynamic steady state non-equilibrium process, which in this sense closely models the conditions inside a cluster source where clusters are removed as fast as new vapour appears).

2.7.   Molecular beam methods: The formation of a cluster beam

Having considered the various factors involved in the formation of clusters, we turn to the question of extracting them from the condensation chamber and forming a good quality beam. This is a very important part of the design of a cluster source, because it is easy with a poor design to disrupt the flow from the nozzle and scatter the beam, so that most of the clusters generated are lost.

2.7.1.   Supersonic expansion and shock waves

As the inert gas and cluster mixture leaves the condensation chamber through the nozzle, the pressure gradient across the nozzle from the inert gas bath at source pressure P_0 to the high vacuum region at P_b accelerates the flow. The degree of acceleration depends upon the pressure ratio P_0/P_b, but if this ratio exceeds a critical value G, given by (Miller, 1988)

$$G = \left(\frac{(\gamma + 1)}{2} \right)^{\gamma/(\gamma - 1)}$$

(2.6)

which is less than 2.1 for all gases, then the flow will become supersonic, that is, the flow velocity exceeds the local speed of sound in the gas and the Mach number $M > 1$. In this case, the situation may be complicated by the formation of shock waves. These shock waves are undesirable because they can cause scattering of the beam, substantially reducing the beam intensity. They occur because the flow must adapt to the boundary conditions downstream, but the speed with which information about downstream conditions may propagate against the flow is the local speed of sound. Thus if $M > 1$, information cannot propagate upstream. Nevertheless, the flow must adapt to boundary
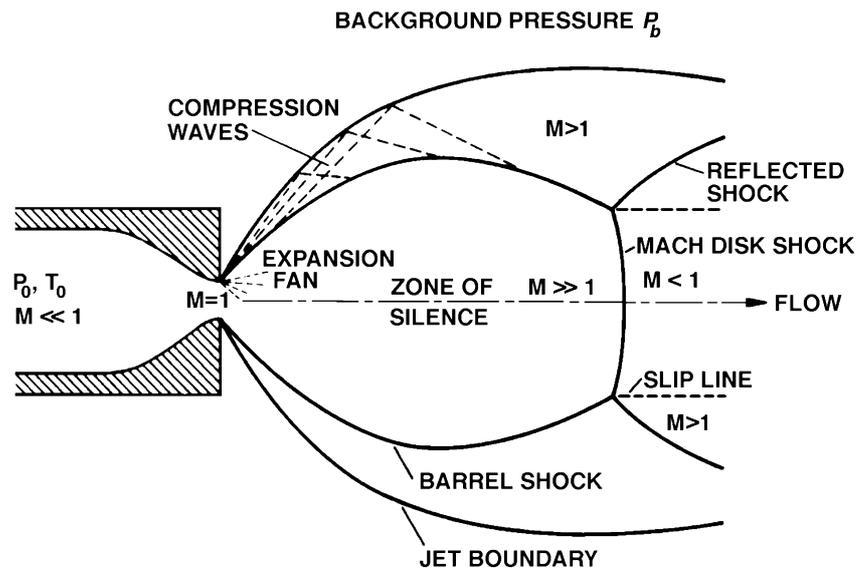
BACKGROUND PRESSURE P_b

COMPRESSION WAVES

EXPANSION FAN

P₀, T₀
M ≪ 1

M=1

ZONE OF SILENCE

M ≫ 1

M>1

REFLECTED SHOCK

MACH DISK SHOCK

M < 1

FLOW

SLIP LINE

M>1

BARREL SHOCK

JET BOUNDARY

Figure 2.5   Continuum free-jet expansion (Miller, 1988).

conditions somehow, and does so by the formation of these shock waves—thin nonisentropic regions of large velocity, pressure, temperature, and density gradients.

Figure 2.5 illustrates the essential features of a supersonic jet expansion into a region of background pressure P_b. The gas accelerates in the nozzle throat to approximately $M = 1$ at the exit and then continues to accelerate and expand further as it moves away from the nozzle. It becomes 'over-expanded' since it does not 'know' about P_b and so must be recompressed by a series of shocks. The Mach disk perpendicular to the flow occurs at a characteristic distance from the nozzle and marks a transition from supersonic flow back to subsonic flow. An experimentally derived correlation for the distance from the nozzle to the Mach disk in nozzle units is given by

$$\frac{x_M}{d} = 0.67 \left(\frac{P_b}{P_0} \right)^{1/2} \tag{2.7}$$

The barrel shock extends from the nozzle to the outer rim of the Mach disk and forms a boundary between the outside region of background pressure and the zone of silence. (The zone of silence is so named because information about conditions outside cannot propagate into it.) Between the barrel shock and the jet boundary is a complicated region of viscous, heat conducting, and nonisentropic flow.

In order to avoid scattering and severe attenuation by the shocks, it is necessary to extract a beam from the zone of silence *before* it encounters the Mach disk. This cannot be done simply by placing an aperture in the zone of silence to select the beam, because the presence of the aperture plate will both set up complex shock waves across the aperture, and reflect off-axis molecules back into the beam causing further scattering. The usual solution is to use a skimmer—a truncated cone with a very sharp leading edge that allows gas to pass through the centre relatively undisturbed, while off axis molecules hit the side

of the cone and are deflected away from the axis. The optimum design of the skimmer depends on the conditions of operation. There are two important regimes of operation.

2.7.2.   The Campargue source

Pioneered by Campargue (1964, 1984) this operates with a relatively high background pressure, $P_b \geq 10^{-2}$ mbar, where Roots pumps are normally used. Under these conditions, the Mach disk is found within a few nozzle diameters of the nozzle, but up to this Mach disk—that is, within the zone of silence—the expansion is just as it would be if it were into a perfect vacuum. The design of the skimmer used to extract the beam from this over-expanded region is critical, since severe shock waves may be set up with such a large background pressure. Campargue (1984) found an optimum angle for the skimmer opening of around 50°. This is a compromise between avoiding scattering off the outside of the skimmer back into the beam, requiring a small external angle, and avoiding scattering off the inside of the skimmer from molecules passing through it, requiring a large internal angle. The problem of scattering inside the skimmer is exacerbated at high pressures due to the attachment of the shock wave to the leading edge of the skimmer, forming a thick boundary layer attached to the skimmer opening (Anderson, 1966) which may significantly reduce the width of free passage through the skimmer.

Advantages of this scheme are that the pumping requirements for a given gas load are much reduced at higher pressure, which leads to an overall reduction in system size. The main disadvantage is the critical design of the skimmer. Another factor that may be of importance is that Roots pumps are noisy, causing system vibration, and more expensive than diffusion pumps.

2.7.3.   The Fenn type free jet

The Fenn type free jet operates in the high vacuum region ($P_b \leq 10^{-4}$ mbar) where, due to the lesser influence of the background gas, the Mach disk is formed much further from the nozzle. Indeed, in some cases no Mach disk is formed at all and the transition from free jet expansion to free molecular flow is smooth. The expansion and acceleration of the gas from the nozzle ceases when the jet becomes too rarefied for sufficient collisions within the jet, and the skimmer is placed somewhere beyond this point. The exact position is often determined by the required angular divergence of the beam. The design of the skimmer is much less critical than in the Campargue source, and an opening angle of around 30° is usually chosen as optimum.

2.7.4.   Free jet expansion

If the skimmer is well designed so that its interference with the expanding jet due to scattering and shocks is negligible, then the flow from the nozzle is considerably simplified and can be treated as a free jet expansion. Given that the expansion is supersonic, that is $P_0/P_b > G$, equation (2.6), then the gas exits from the nozzle at a pressure of P_0/G, independent of the background pressure, and continues to expand. Miller (1988) gives an in depth description of the continuum fluid mechanics treatment
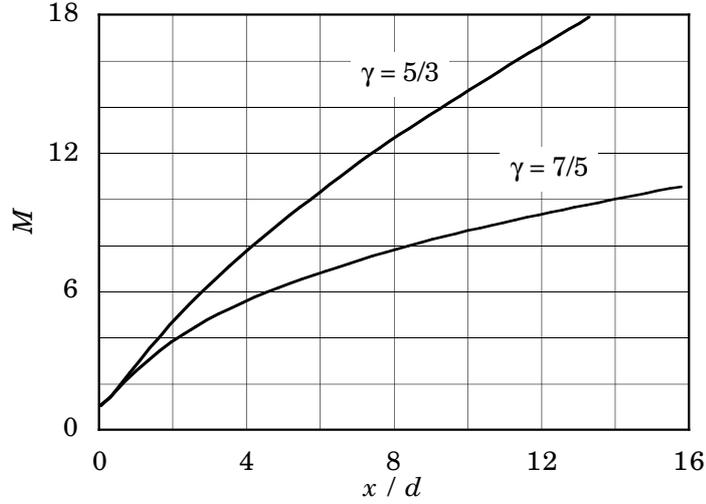
Figure 2.6   Centre-line Mach number dependence on γ, axisymmetric expansion (after Miller, 1988).

used to model the expansion, and here it will be sufficient to point out a few of the most important features.

It is possible, from thermodynamic and continuum flow considerations, to calculate M as a function of position relative to the nozzle and to fit analytical forms to the results (figure 2.6). From this, the other properties of the beam such as temperature, density and collision frequency may be deduced from the following relations:

$$\frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-1} \tag{2.8}$$

$$V = M \sqrt{\frac{\gamma R T_0}{W}} \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-1/2} \tag{2.9}$$

$$P/P_0 = \left(T/T_0\right)^{1/(\gamma - 1)} \tag{2.10}$$

(2.8) and (2.9) are exact relations, whereas (2.10) is for an isentropic, ideal gas expansion with γ = constant. T_0 is the source temperature, and W is the molecular weight of the gas. Figure 2.7 shows how in the initial part of the expansion the velocity V increases rapidly to reach 98% of V_∞, the terminal velocity, within the first several nozzle diameters. The temperature though falls more slowly, and as the expansion continues and the collision frequency drops there comes a point at which there are not enough collisions to maintain equilibrium between the various energy modes of the beam. From here the continuum fluid mechanics description breaks down and the beam properties become frozen in. For example, beyond this point, the translational temperature of the molecules' motion perpendicular to the beam will be different to that parallel to the beam. Although strictly the transition region is gradual, a useful approximation is to consider a *quitting surface*
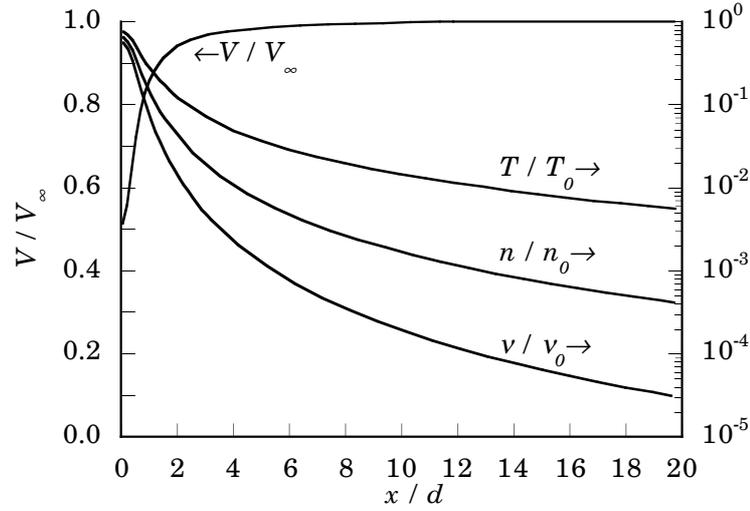
Figure 2.7 Free jet centre-line properties versus distance in source diameters; $\gamma = 5/3$; temperature—T, density—n, and binary hard sphere collision frequency—v are normalised by source stagnation values T_0, n_0, v_0 (Miller, 1988).

(Beijerinck 1981), a hypothetical surface that separates the continuum isentropic region from the free molecular region. It is defined as the surface at which the Mach number reaches the terminal Mach number. It can be thought of as a virtual source, which enables predictions of beam profile downstream and the effect of the finite skimmer aperture to be made. The terminal Mach number is given by Miller (1988) as

$$M_\infty \approx \sqrt{\frac{2}{\gamma}} A \left[\sqrt{2} n_0 d \left(\frac{53 C_6}{k T_0} \right)^{1/3} \right]^B \tag{2.11}$$

For a monatomic gas $\gamma = 5/3$, $A = 0.527$ and $B = 0.545$. $53 C_6 / k T_0$ is a cross-section, and n_0 is the gas number density in the source.

It has been found that the shape of the nozzle has little effect on the expansion. The sonic surface (the surface over which $M = 1$) at the exit of the nozzle is convex for a sharp edged orifice, and concave for a capillary tube. The exact shape slightly modifies the flow field in the first nozzle diameter of the flow, but beyond this its effect is negligible.

2.7.5.   Mixed beams: velocity slip

In mixed beams, in which a small concentration of a heavy species is introduced, the heavy molecules may be accelerated up to the same speed as the lighter molecules, in some cases gaining a kinetic energy of several electron volts. However, if the heavier species is a great deal heavier than the lighter species and source pressure is relatively low, *velocity slip* will occur, in which the collision process does not accelerate the heavier molecules sufficiently. This is most likely to occur within regions of large pressure gradients, such as in the subsonic region of the nozzle and in the first nozzle diameter of

Parameter	Value
μ_{ij}	6.4×10^{-27} kg
$\overline{m}$	4.1×10^{-26} kg
$n_0 d$	9.6×10^{19} m
$\sigma_{ij}^2 \Omega_{ij}^{(11)*}$ (Ar)	6.9×10^{-20} m^2
$\sigma_{ij}^2 \Omega_{ij}^{(11)*}$ (Ag$_{100}$)	1.1×10^{-18} m^2

Figure 2.8 Parameters used in equation (2.12) for a 0.06% Ag_{100} in He mixture.

the flow. This effect will be important when mass-selecting the beam, since it can introduce a significant mass dependent energy variation of up to a few eV.

The velocity slip parameter is defined as (Miller, 1988)

$$VSP \equiv \frac{\sqrt{\mu_{ij}\overline{m}}}{\left|m_j - m_i\right|} n_0 d \ \sigma_{ij}^2 \Omega_{ij}^{(11)*} \tag{2.12}$$

where μ_{ij} is the reduced mass, $\overline{m}$ is the mole fraction average mass, n_0 the number density inside the source and d the diameter of the nozzle. $\sigma_{ij}^2 \Omega_{ij}^{(11)*}$ characterises the collision interaction between the molecules.

As an example of the amount of velocity slip expected in an inert gas condensation cluster source, we use this formula to calculate the VSP for Ag_{100}. Figure 2.8 gives the values for the parameters used. Since no data for $\sigma_{ij}^2 \Omega_{ij}^{(11)*}$ for Ag_{100} is available, the value for Ar is used, scaled by the ratio of the cross-sectional areas for Ag_{100} and Ar. The VSP in this case is 0.09. Using

$$\frac{\Delta V}{V_{\infty,isen}} \approx 0.5\left(VSP\right)^{-1.07} \tag{2.13}$$

we obtain $\Delta V/V_{\infty,isen} \approx 6$. This large value indicates that the clusters are hardly accelerated by the helium beam at all, and so emerge with only thermal energies. (Contrast this with a typical expansion of 3% Ar in He mixture where the VSP = 14 and $\Delta V/V_{\infty,isen} \approx 0.03$.) In terms of the mass selection of the cluster source, it means that the heavier clusters in the ion beam will have the same energy as the lighter clusters, as required for mass selection. Had the VSP been much larger, an allowance would have been needed in the calibration of the mass filter for the extra kinetic energy of the more massive clusters.

Another interesting effect in mixed beams is that of mass selectivity along the axis of the beam. Within the isentropic region of the expansions, all the particles acquire the same translational temperature perpendicular to the beam, $T_\perp$, and the same velocity in the direction of the beam (ignoring velocity slip). The perpendicular velocity ratio is then given by $V/\sqrt{2kT_\perp/m}$, which implies that lighter species tend, on average, to drift away from the centre of the beam more quickly. It might also be noted that velocity slip will tend to reduce this effect and it is unlikely that it would be very large in an inert gas condensation source.

We will return to consider some of the points raised in this survey in greater detail in chapter three, where I shall describe the design and performance of the cluster source used in the experiments described in this thesis.

2.8.   References

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