

SPECIAL TOPIC: HELIUM NANODROPLETS

Experimental studies of helium droplets

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In this report I will review experimental studies of free helium droplets, with the exception of spectroscopic studies of helium droplets that contain impurities. This particular topic, as well as theoretical studies of helium droplets, will be reviewed separately elsewhere in this issue. © 2001 American Institute of Physics. [DOI: 10.1063/1.1418249]

I. INTRODUCTION

There are at least as many stated *a priori* motives for generating and studying helium droplets as there are experimenters who have tried to do so. I would guess that more often than not, however, the underlying idea has been simply “let’s see what happens—it’s certain to be interesting, and probably surprising.” The system surely has not disappointed us in that regard. In the present context, by “droplet” I mean any condensed helium system characterized by the lack of contact with any material body other than possibly its own vapor. The sizes accessible by various experimental techniques range continuously from levitated centimeter scale droplets containing 10^{22} atoms to helium dimers in a molecular beam. Their description as a droplet is appropriate because helium, unique among materials, has no triple point. The liquid can coexist with its vapor all the way to absolute zero. Therefore cooling by evaporation in a vacuum must result in a liquid rather than a solid structure. Of course, there is the interesting question of what it means to be a liquid when the number of atoms in the system becomes very small. It is an even more challenging question when the droplet is charged and thus has a solid core.

The problems in the case of helium are made even more interesting by the fact that there are two stable isotopes, one a boson (^4He) and the other a fermion (^3He). These two systems have completely different characteristics at low temperatures. In the temperature range accessible by evaporative cooling, ^3He behaves in most ways as an ordinary fluid but ^4He enters a macroscopically ordered liquid state which is characterized by the property of superfluidity. This property historically has been operationally defined by various relatively macroscopic measurements. It will be very instructive to learn what superfluidity means in a system so small that these conventional definitions cannot apply. The properties of superfluid helium are strongly influenced by the existence of solid boundaries even for macroscopic systems, however. This is particularly evident in the case of rotating systems. Some of these and other related questions are beginning to be answered by experiment, but others remain wide open.

My objective in this report is to review the evolution of experimental studies of helium droplets, with the exception of spectroscopic studies of captured impurities, which are the subject of separate reviews elsewhere in this issue. The approach will be relatively noncritical. I will attempt to provide a guide to past and present literature in the field rather than a didactic presentation of our present understanding of the subject. Most of these studies, particularly the earlier ones, were undertaken with the goal of discovering the kinds of experimental questions that could be asked of this very difficult system, rather than of answering questions that were well posed in advance of the experiment. As a consequence, finding the threads which connect these experiments is not easy, because several of them are pretty short! I have chosen to divide them into three groups: First, there are those experiments designed to study droplets whose size is large enough so that in principle they could be seen in an optical microscope. Second, at the other end of the size range, there are experiments in which charged nanodroplets and clusters containing fewer than 100 atoms are produced by inhomogeneous nucleation in low temperature helium vapor. Finally, there are experiments in which droplets are produced by homogeneous nucleation in helium nozzle expansions. These range in size from dimer molecules up to micron scale clusters. Most current interest appears to lie in this area, and the major part of this review will involve describing these experiments. Within this latter group, I have divided the discussion by the particular techniques used to study the system. Since in many cases several techniques are combined in a single experiment this means that often a particular report will be cited in several categories. I hope that this will prove helpful to others who are contemplating the application of one of these methods in a future experiment. Finally, while the words nanodroplet and cluster have been used often to describe particularly the smaller helium droplet systems, I will make no distinction among these terms in what follows.

II. VERY LARGE HELIUM DROPLETS

It is highly likely that the earliest observation of helium droplets was one described by Kamerlingh Onnes. In a Joule “free expansion” experiment which he performed¹ in 1908,

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several months before he first liquefied helium by the Joule–Kelvin process,² he noted that when he carefully removed H₂ impurities before expanding the gas, “a thin cloud appeared and vanished extremely rapidly (in 1 [s] nearly). The mist now had another aspect.”

Helium droplets large enough to be observed by optical means have continued to be a subject of active investigation in recent years. In most cases the objective has been to levitate the drops in electric and magnetic fields. In experimental studies of the magnetic levitation of nominally neutral superfluid droplets by Maris, Seidel, and their collaborators,^{3–6} formation has been accomplished by several methods. Helium mists were generated by rapid cooling of the experimental cell, or by rapid pumping on the liquid below the trapping volume, and larger droplets were formed through coalescence. Most of the time, droplets were introduced directly through capillaries, however. The size of the droplets under study in their experiments was rather large, in the 1 mm to 1 cm range, and they directed their interest primarily to visual studies of the oscillation dynamics^{6,7} and to the recombination of larger droplets.^{3–5} Studies were also made of the laser levitation of helium droplets in the 10 μm size range.⁸ In this case the droplets were produced by using a focused hemispherical piezoelectric transducer driven strongly a few millimeters below the surface. A fine mist of microscopic droplets was ejected from the liquid. Some were captured by the laser trap, where studies were made of their evaporation rate. They also mentioned that when the drive voltage was further increased, it was possible to produce a fountain of larger droplets ($\approx 500 \mu\text{m}$) emerging from the liquid at the acoustic focus. Most recently, Williams and collaborators⁹ have described a method of generating a superfluid fog over a several centimeter region by driving a piezoelectric transducer plate immersed under liquid helium. The particle size could be controlled by the acoustic frequency, and ranged from 10 to 100 μm in their experiments. The fog density ranged from 10³ up to 10⁸ droplets/cm³.

Charged helium surfaces in a strong electric field can become unstable and emit multiply charged droplets, as observed by Dahm and Boyle.¹⁰ The characteristic size of these positively charged drops was believed to be $\approx 200\text{--}600 \mu\text{m}$, although the droplets were not directly observed. Charged superfluid helium droplets with a characteristic size of 100 μm also have been generated and dynamically levitated using electric fields by Niemela.¹¹ He utilized a method of producing positively charged droplets for these experiments in which they fell from a sharp electrode which was supplied with liquid in a controlled way by a fountain pump. He also mentioned a method of producing a “fountain” of charged droplets by operating a field emission point just below the liquid surface.

While most of the above-described studies have involved droplets in the size range above 10 μm ($\sim 10^{13}$ atoms), this may not represent limitations inherent in the methods of droplet production, but instead, in the optical methods that have been used to observe them.

III. SMALL CLUSTERS FORMED ABOUT CHARGES IN HELIUM VAPOR

At the other end of the size range, nanodroplets have been created by inhomogeneous nucleation about positively charged particles in low temperature helium vapor, directly forming He_N⁺, or (I)He_N⁺ ions, where I is an impurity. Patterson¹² first reported the existence of the He₃⁺ ion in mobility studies at low temperatures and determined its dissociation energy. He₃⁺ and He₄⁺ ions were found in mass spectrometric studies of plasmas in isotopic mixtures of helium by deVries and Oskam¹³ (at 80 K) and by Gusinow *et al.*¹⁴ (at 300 K). Dahm and Sanders¹⁵ measured the effective mass of the positive ion in He vapor at 4.2 K by ac-mobility techniques and found a value of about 75m_{He}. Henson¹⁶ also found qualitative evidence for clustering in dc-mobility measurements in the saturated vapor. In a series of experiments, Akinci and Northby^{17–20} studied the pressure ($P/P_{\text{sat}}=0.1\text{--}1$) and temperature (1.3–4.2 K) dependence of the ion droplet mobility. By modeling the scattering of vapor atoms from the charged droplet they showed that the radius of the droplet ranged from 7 to 9 Å ($N \sim 32\text{--}68$ atoms) and could be calculated correctly by the classical thermodynamic formula of Thompson.²¹

Kobayashi and collaborators have studied the formation of single shell cluster ions ($N \leq 15$) in a liquid helium cooled drift tube at low pressures. They examined condensation about He⁺,²² other rare gas impurities,²³ and various molecular impurities.^{24,25} They have made qualitative studies of the stability of these ions and, in the case of pure helium ions, have shown that there are large reductions in the stability between $N=3$ and 4, $N=10$ and 11, and $N=14$ and 15. The reduction between 3 and 4 also has been observed by Hiraoka and Mori.²⁶ They suggested that these small single shell clusters are solid, and proposed a geometric explanation of the special stability at $N=10$ and 14.

IV. DROPLET NUCLEATION IN NOZZLE EXPANSIONS

The most common method used to produce helium droplets is through homogeneous nucleation in supersonic nozzle expansions.²⁷ Helium gas, initially at rest in a stagnation region at a temperature T_0 and pressure P_0 , expands through an orifice into a differentially pumped vacuum system. The expanding gas accelerates and cools adiabatically. If its local thermodynamic state passes into the coexistence region before internal collisions effectively cease, phase separation will take place leaving a mixture of droplets and vapor. The mixture is collimated by a conical skimmer and a helium cluster beam is formed.²⁸ Beam formation is straightforward, but because helium is especially inert, the search for suitable experimental methods of learning about this system has been anything but straightforward. Early experiments were exploratory, and more often determined by what the experimenters *could* measure, rather than what they *wanted* to measure.^{29,30} I have organized this part of the review about the experimental methods used to date, and will try to illustrate the development of the use of each of them. It is safe to say that, with two exceptions, all studies involve causing the droplet to interact with one or more local probe particles or excitations,

and then (usually) studying the behavior of the combined system. The exceptions involve experiments in which the beam is modulated, temporally and spatially, by interaction with surfaces, and are otherwise nondestructive in nature. These have involved chopped beam time-of-flight (TOF) experiments to measure beam velocity distributions, and more recently, in combination with transmission diffraction gratings, to measure the mass distribution of the smallest clusters. I will treat these methods first. Other methods all involve interaction of droplets with atoms and molecules, with electrons,³¹ or with photons, or with various combinations of them. As noted previously, this review explicitly excludes the method of spectroscopy of captured particles. The other methods will be discussed in turn.

A. Chopped beam time-of-flight measurements

The first experiment which detected condensation in a helium nozzle expansion, by Becker and collaborators^{32–34} in 1961, involved a mechanically chopped TOF measurement. They expanded helium gas through a converging 150 μm diameter nozzle from $T_0 = 4.2$ K and $P_0 = 0.98$ bar and obtained a very narrow velocity distribution peaked at 165 m/s. The narrowness of the observed distribution could be explained only by cluster formation.³⁵

While several experiments have included provision for measurement of the velocity, the only systematic studies of the velocity distribution in condensing nozzle beams over a wide range of source conditions have been those of Toennies and collaborators.^{29,30,36–41} The central references are the papers by Buchenau *et al.*³⁰ and Harms *et al.*⁴¹ In Ref. 30, the condensed nozzle beam was mechanically chopped and, after a flight path of over a meter, the beam was crossed by an electron beam. The He_N^+ ions produced were mass analyzed and their separate time-dependent signals were correlated with the chopper. The nozzle was in most cases a 5 μm sonic nozzle which permitted using significantly higher pressures than noted previously (8–20 bar). Temperatures were varied between 5 and 20 K. At 20 bar and 20 K only one TOF peak was observed, but as the temperature was decreased the TOF distribution measured with He^+ split into four separate peaks. These subsequently were interpreted as derived from a beam consisting of an atomic component (the fastest), and two separate coexisting cluster components. The slowest component consisted of the largest clusters, and was responsible for two of the observed TOF peaks in the detected signal. One involved charged and the other metastable excitations. The intermediate TOF peak was assigned to a smaller cluster component. They presented measurements of the pressure and temperature dependence of the mean speed and speed ratio of the separate peaks, where they could be identified. In their data at 20 bar they identified three qualitatively different experimental regimes: a high temperature regime where only one TOF peak was present, a second, where a slower cluster peak could be identified, and a third, where two cluster peaks could be seen. The boundaries between these regimes were not sharply defined, however.

The phase diagram³⁹ of bulk helium plays a very important role in their interpretation of the results. The local state of the adiabatically expanding gas is expected to follow an

isentropes and the nature of the phase separated system which results should depend strongly on where that isentropes crosses into the coexistence region. In particular, since the stagnation entropy can be below the critical point entropy at low temperatures, the system before separation is described more appropriately as a (superheated) liquid than as a (supercooled) vapor. The separation process then is better described as flashing or cavitation than condensation. (I will refer to clusters formed in this way as “fragmentation clusters” in what follows.) They divided the phase diagram into three regimes: (I) where the isentropes cross the phase boundary from the gas phase, (II) where the isentropes pass “near” the critical point, and (III) where the isentropes cross from the liquid phase. They also pointed out the significance of whether the phase boundary is crossed before (subsonic) or after (supersonic) the system passes the nozzle. They discussed their results in terms of this separation of the phase diagram, but the boundaries were not sharp and the detailed connections are a bit murky.

Harms *et al.*⁴¹ extended these measurements to stagnation conditions which were in the immediate vicinity of the critical point. The main objective of this work was to find suitable conditions for producing large slow droplets. They reported finding speeds as low as 45 m/s for $P_0 = 1.5$ bar and $T_0 = 3.5$ K. They also observed that there was a single cluster TOF peak in this region, but that there were decided anomalies in its properties as the stagnation state moved along an isobar passing very near the critical point. In particular, there was a discontinuity in the velocity and a minimum in the speed ratio at the critical point. They also mentioned that size measurements, of the type described by Lewerenz *et al.*,^{42–44} showed that for this isobar (2.3 bar) the cluster size increased rapidly with decreasing T_0 from $\sim 10^3$ atoms at 6.5 K to $> 10^5$ atoms at 5.3 K.

B. Interaction of cluster beams with transmission gratings and surfaces

Schöllkopf and Toennies^{45,46} were the first to use nanostructured transmission gratings to study the diffraction of a helium nozzle beam. They recognized that since the velocity distribution of nozzle beams containing atoms and small clusters is very narrow, the deBroglie wavelength of a cluster will be inversely proportional to the number of atoms it contains. Thus each cluster size will diffract at different angles when it passes through the grating. They studied diffraction by a grating with 200 nm period and clearly identified diffraction peaks corresponding to He_2 and He_3 clusters. This was the first unambiguous proof of the existence of the extremely weakly bound He_2 cluster/molecule (see, however, Refs. 47–49).

Luo, Giese, and Gentry⁵⁰ studied the transmission of beams containing atoms and dimers through various nanoscale sieves, whose hole sizes ranged from 98 to 410 nm. The dimers were presumed destroyed by contacting the surface and since they were much larger than individual atoms they were less likely to be transmitted by the sieve. By observing the relative transmission coefficients of the atomic and dimer components they found the mean internuclear distance in

He₂ to be 62 ± 10 Å. This may be only an upper limit, however.^{51,52}

Grisenti *et al.*^{53,54} carefully modeled the velocity dependence of the effective He and He₂ slit widths found in diffraction experiments from a 100 nm period grating. They extracted a value of 52 ± 4 Å for the molecular bond length, and a binding energy of about 1.1 mK.

Most recently, these diffraction studies have been extended to study the tetramer cluster as well.^{54,55} The authors are now able to study the way concentrations of the three smallest clusters evolve in a nozzle beam as a function of the source conditions. This essentially nondestructive method opens up the possibility of making truly detailed studies of the onset of condensation and of providing experimental tests of classical theories of homogeneous nucleation.

In another related use of their diffraction grating, Schöllkopf *et al.*⁵⁶ have shown that by rotating the grating about an axis parallel to the slits, they could make a variable size cluster nanofilter which was capable of selecting and manipulating large helium clusters in the size range from $\sim 10^4$ to $\sim 10^6$ atoms. The results agreed well with previous mass distribution measurements at high and low temperatures, but showed deviations to larger sizes for expansions which pass near to the critical point.

Finally, in the general context of surface interactions, the early surface reflection experiments by Gspann and Krieg⁵⁷ and the recent studies of the surface ionization of alkali doped clusters by Stienkemeier *et al.*⁵⁸ also should be mentioned.

C. Particle bombardment of pure clusters

In principle, one of the most direct ways to probe the structure and properties of helium clusters is to scatter atoms from them and observe the results. In actuality, it is quite difficult to extract the kind of information about the clusters that one might wish from such experiments. The result is invariably a convolution, involving *a priori* unknown size distributions, as well as unknown capture and detection processes, which are all simultaneously under investigation. Nonetheless, much effort has been expended on such studies, and much progress has been made. These studies have been carried out by Gspann and collaborators in Karlsruhe, and by Toennies and collaborators in Göttingen.

The earliest studies of particle bombardment of helium clusters were those of Gspann *et al.*^{59–66} These studies have also been the subject of a more recent review.³⁵ The first experiments^{59,60} involved measuring the depletion of a beam of cesium atoms when it crossed a helium cluster beam. Cs had the advantage that it could be detected with a surface ionization detector. The extinction cross section for the crossed beam was strongly influenced by the atomic background, however, and no detailed conclusions were drawn. These extinction experiments were later revisited⁶³ with much improved collimation. The results led them to conclude that the incident atoms did not pass through the clusters. The next experiments^{61,62,64} involved measurement of the deflection of the He clusters by a cross jet of Xe or CO₂. Comparative measurements with ⁴He_N and ³He_N clusters

could be made for the first time. They found, for both types of clusters, that the momentum of the scattering atoms geometrically intercepted by the clusters was not completely transferred to them. They argued that this could be explained by deep penetration of the impurity followed by anisotropic ejection of helium atoms. They also examined the possibility that the low momentum transfer is a signature of the vanishing viscosity associated with superfluidity.⁶⁴ This is a bit of a puzzle, however, since there appears to be no major experimental difference between the different isotopes.³⁵ The final set of experiments^{65,66} again involved Cs scattering from clusters, but in this case they included a second surface ionization detector which allowed them to detect Cs anywhere in the scattering plane. The only Cs they found, other than that in the direct Cs beam, was in the precise direction of the cluster beam. Further experiments⁶⁵ indicated that the cesium moving in the direction of the clusters also had their precise velocity. Thus they argued that the incident cesium was actually bound in or on the clusters. A good overview of these experiments is given in the review by Gspann.³⁵

The next series of particle bombardment studies has been carried out by Toennies and collaborators.^{41–43,67–72} The evolving apparatus permitted several types of measurements in a single device, but not all were used in each experiment. There was a standard helium cluster beam source containing a 5 μm sonic nozzle (with an aspect ratio of ≈ 4 ^{41,69}), with T_0 and P_0 variable over a wide range. Beams of both isotopes of helium could be produced and mechanically chopped for TOF studies. There were two⁷³ methods by which the beam could interact with scattering atoms and molecules: there was a scattering chamber with collimating apertures through which the clusters passed, and which could maintain a locally increased pressure of a scattering gas, and there was a room temperature collimated atomic or molecular beam which intersected the cluster beam at a fixed angle in an interaction region 60 cm from the source. The detector assembly could be rotated about this point, and had provision for electron bombardment of either the cluster beam with mass analysis of the fragments, or of the gas particles when the detector was operated as a stagnation (partial) pressure gage. The first experiments, reported by Scheidemann *et al.*,^{67,68} described conclusive evidence of the stable capture of several atomic and molecular species. In an experimental study of the pickup of neon atoms by ⁴He_N clusters they studied the dependence on stagnation conditions of the capture and detection of atomic Ne. There was a strong correlation with the stagnation entropy, which indicated that the process peaked strongly in the vicinity of the critical isentrope.⁷⁴ They suggested that clusters formed by expanding through the critical point had different properties than others.⁷⁵ The next experiment, by Lewerenz *et al.*,⁴² measured the deflection of ⁴He_N clusters associated with capture from the crossed beam of SF₆ particles with well-defined momentum. The studied moderate sized ($< 2 \times 10^4$) clusters formed by condensation, and operated under single collision conditions. By detecting the signal of the SF₅⁺ ion fragment, they were assured that all its momentum was captured by the droplet.⁷⁶ Thus they could infer the droplet size distribution directly from the angular distribution of the deflected clus-

ters. The size distributions measured in this way were log-normal, with a half width comparable to the average size. Since they were not affected by the major fragmentation uncertainties associated with ionized cluster mass measurements, they provide the best information about the size of condensation clusters presently available.⁷⁷ In a second paper, Lewerenz *et al.*⁴³ (see also comments^{44,78}) concentrated on the process of multiple capture of foreign atoms as the cluster beam passed through the scattering chamber, and on their subsequent coagulation inside the clusters. One major conclusion (that of negligible fragmentation of embedded foreign atom clusters upon ionization) followed from their observation that the size distribution of pure foreign atom fragment ions agreed with the predicted Poisson distribution for multiple capture. Another conclusion was that only a fraction of the foreign atoms which collided with clusters were captured and delivered to the detector,⁷⁹ even though all their energy and momentum had been delivered to the cluster in the collision. Harms *et al.*⁶⁹ have utilized scattering measurements to determine the average density of ${}^4\text{He}_N$ clusters. The mean number of atoms in a cluster was measured by deflection experiments, as was done earlier. The integral cross section for clusters was measured by the attenuation of the direct cluster beam caused by secondary beam scattering. The cross section was calculated to be geometrical, with a radius equal to the point at which the density has dropped to 1% of the central density. The average density extracted from these data was significantly less than the bulk liquid density. This density defect results from the diffuse surface profile, and can be used as a measure of the thickness of the surface layer. The results agreed well with theory, and suggested a surface thickness of 6–8 Å. In a second paper,⁷² these studies have been extended to ${}^3\text{He}_N$ clusters. Finally, Harms and Toennies^{70,71} have studied the transmission of quite large ($N \approx 1.5 \times 10^9$) and slowly moving (≈ 75 m/s) ${}^4\text{He}_N$ clusters through a scattering chamber filled with either ${}^3\text{He}$ or ${}^4\text{He}$ gas. ${}^3\text{He}$ atoms were found to transfer a significantly smaller fraction of their momentum and energy to the cluster than ${}^4\text{He}$ atoms. This was consistent with the idea that lower energy ${}^3\text{He}$ atoms did not satisfy the Landau criterion for creation of excitations in the superfluid ${}^4\text{He}_N$ droplet and thus were transmitted without loss of momentum and energy.

D. Electron bombardment of pure clusters

As noted previously, ionization of cluster beams is involved in the detection process in the overwhelming majority of experiments which we will describe. In the following I will discuss primarily those experiments which attempt to learn about the nature of these charged particles and clusters, and not those that simply use them to detect the presence of neutral clusters.

1. Positively charged cluster ions

One of the earliest publications which describes the size of helium droplets charged by electron bombardment is by Gspann *et al.*⁵⁷ In experiments involving reflection of helium clusters from surfaces, Gspann *et al.* used an in-line accelerating field TOF technique to characterize the mean size-to-charge ratio of the positively charged clusters produced by

bombarding their neutral cluster beam with 190 eV electrons. He found $N/Z \approx 1 \times 10^5$ for his source conditions of ≈ 4.2 K and ≈ 0.9 bar. The nozzle used in these experiments was cylindrical, with an aperture of 100 μm and an aspect ratio of 5. Becker, Gspann, and Krieg⁵⁹ also quote a size of 6.5×10^6 atoms measured by the same technique. The source contained a converging-diverging nozzle but no other information was included about stagnation conditions.

The next description of positive helium cluster ions was given by van Deursen and Reuss.⁸⁰ They used a magnetic mass spectrometer to detect small charged clusters and studied primarily the pressure dependence of their appearance in the condensation threshold region. They measured sizes up to He_{13}^+ at 7K and 1.5 bar with a 6 μm nozzle, but it seems likely that these fragment ions came from even larger neutral parents.

Gspann and collaborators, in a further series of publications,^{62,81–84} described measurements of large He_N^+ cluster ions of both ${}^4\text{He}$ and ${}^3\text{He}$, whose sizes were in the $N \sim 10^5 - 10^7$ range. Evidence of large multiply charged clusters was also presented.⁸² They used a converging-diverging nozzle with a ≈ 100 μm orifice,⁸⁴ which was typically held at a temperature of 4.2 K for ${}^4\text{He}$ and 3.2 K for ${}^3\text{He}$. No information about source pressure was given. It is quite certain that these clusters were formed by condensation, however. Their most surprising observation was that there was a preferred size of “minicluster ion” which was present after electron bombardment of large clusters. The mean size was $N \approx 68$ atoms for ${}^4\text{He}$ and 85 atoms for ${}^3\text{He}$. They ascribed the ejection of these ions to the release of electrostrictive polarization energy in the vicinity of an ion which formed near the droplet’s surface, and they accounted for the sizes quantitatively in an equilibrium model. While double ionization of the parent cluster had an effect on the yield, they rejected the idea that Coulomb repulsion between charges in a doubly ionized cluster played a fundamental role in their formation.⁸⁴ More recently, Gspann and Ries,⁸⁴ have extended these experiments to study the formation of clusters as the source temperature passes through the λ point. In this case, clusters are formed by condensation directly into the superfluid phase. Most properties of the beam are continuous at the transition. The sole exception is the total beam flux, which exhibits an anomalous behavior. The authors attribute this to the formation of a (mobile) film in the nozzle below T_λ .

Stephens and King⁸⁵ formed cluster beams from both isotopes of helium by expanding from 4.2 K and 0.53 bar (for ${}^4\text{He}$) and from 3.2 K and 0.73 bar (for ${}^3\text{He}$) through a 5 μm pinhole. The beam was ionized by electron impact, and the resulting He_N^+ mass distribution was studied with a quadrupole spectrometer. They observed “magic number” structure in the mass range up to $N = 50$, with locally strong peaks at $N = 7, 10, 14$, and 30 for both isotopes, which they attributed to relative ionic stability. They also studied the region of condensation onset and found very significant isotopic differences. They suggested these differences originated in the fact that ${}^4\text{He}$ dimers are stable while small ${}^3\text{He}$ clusters are not. Similar studies of the small cluster ions formed from beams

near threshold have recently been reported by Pedemonte *et al.*⁸⁶ as well.

The next experiments involving ${}^4\text{He}_N^+$ ions were described in a series of papers by Toennies and collaborators,^{29,30,36–38,40,87} which have been mentioned already in the discussion of TOF measurements. These experiments permitted studies of the mass distribution and the appearance potential of various separate small charged fragments as a function of the source conditions. If very large charged fragments were present, however, they could not have been observed. When condensation clusters were formed³⁰ by expanding along the same isentrope used by Stephens and King,⁸⁵ they observed a very similar “magic number” structure. It also was comparable to the ion stabilities found by Kobayashi *et al.*²² When ions were produced by bombarding fragmentation clusters, the He_4^+ signal (and to a lesser extent He_2^+) rose sharply from obscurity in the mass spectrum. Appearance potential studies⁴⁰ showed that He^+ and He_2^+ were produced from fragmentation clusters at a bombarding energy of about 20 eV, which was near the threshold for producing metastable helium atoms (He^*). He_4^+ ions, on the other hand, required roughly twice that energy. Ions produced from condensation clusters, however, required an energy slightly greater than the atomic ionization threshold. Buchenau *et al.*⁴⁰ suggested that, when bombarding fragmentation clusters, metastable excitonic states could act as an energy storage mechanism and permit ionization by multiple electron impacts. Multiple collisions would be less likely for smaller condensation clusters, so energy storage would be irrelevant. He_4^+ production seemed to require two excitations produced by the same electron. It was suggested that the ion evolved from the combination of two excitons, or from a quartet hole–exciton pair which might lead to the ejection of a metastably excited He_4^{*+} fragment. The later model was supported by optical fragmentation studies by von Issendorff *et al.*,⁸⁷ which showed that this ejected ion was indeed metastable.

Callicoatt *et al.*⁸⁸ have carried out very careful measurements of the small cluster ions formed by bombardment of a beam condensation clusters. The mean size of the precursor clusters was controlled and varied from $N=600$ to 15 000. They observed ${}^4\text{He}_N^+$ ions out to $N=135$. They confirmed the smaller “magic numbers” 7, 10, and 14 found by others, and emphasized the importance of the He_2^+ fragment ion as well. Additional structure was observed out to higher masses but they did not indicate any significant peak at $N=68$, the location of Gspann’s⁸⁴ minicluster ion. They found that relative ion yields became insensitive to the cluster size for larger clusters, and also found the electron energy appearance threshold for most small ions to be close to the ionization potential for bare helium. The mechanism of formation of these cluster ions was discussed at length and it was argued that they were ejected by a nonthermal process. Larger charged fragments, if they were present at all, could not have been seen.

Northby and co-workers^{89,90} were the first to study the large cluster ions produced when bombarding fragmentation clusters. They utilized a stopping potential method which, when combined with velocity measurements, permitted de-

termination of their mass distribution as a function of source conditions. They found that there was a sharp threshold for the onset of large positive cluster ions, and that the mass distribution at lower temperatures fell off exponentially at large masses, extending to beyond $N=10^6$. The threshold correlated well with a value of the source entropy of 6.4 kJ/kg K.⁹¹ They also observed that the size distribution was bimodal in the vicinity of threshold. The two coexisting groups were assigned to condensation clusters ($N < 4 \times 10^3$) and fragmentation clusters ($N > 4 \times 10^4$). The low mass cut-off of the fragmentation group was unexplained.⁹²

Fárník *et al.*⁹³ have compared the production of large charged positive and negative ions from beams which were near or beyond the threshold for fragmentation cluster formation. By studying the electron current dependence of the signal in a deflection energy analyzer they determined that the measured size distributions were affected by multiple charging of positive clusters, and most interestingly, that there was a threshold size below which a doubly positive charged cluster was unstable. They modeled this effect and concluded that the observed threshold, 2×10^5 , implied that such a cluster fragmented asymmetrically, with the smaller charged fragment having a size of roughly 50 atoms. The correspondence of this size to that of Gspann’s minicluster ions was noted, even though he explicitly argued against such a model.⁸⁴

The most recent discussions of positively charged clusters is that of Henne and collaborators.^{94–96} They described careful measurements of the size distribution of positive cluster ions produced from fragmentation clusters by combined deflection energy analysis and TOF measurements. The most essential difference between these measurements and those carried out previously^{89,90} was that increased detector sensitivity permitted orders of magnitude lower ionizing currents. This in turn eliminated multiple charging effects. By assuming negligible mass loss upon ionization, together with an overall ionization and detection efficiency proportional to the area of the cluster, they could extract the same precursor neutral cluster distribution from both positive and negative cluster ion distributions. They proposed a scaling relation and use it to correlate the temperature and pressure dependence of the mean neutral fragmentation cluster size. The distribution itself decayed exponentially at large masses, in contrast to condensation clusters whose distribution is log-normal.⁴²

2. Metastably excited cluster ions

Metastable excitation of ${}^4\text{He}$ and ${}^3\text{He}$ nanodroplets by electron bombardment was first described by Gspann.^{62,81–83} Excited droplets were identified by their ability to release secondary electrons at the first dynode of an electron multiplier when incident at thermal speeds, and after a flight time of about a millisecond after excitation. His principal method of measurement was an in-line ion time-of-flight mass spectrometer. He was able to show that under his source conditions, clusters which were simultaneously positively charged and metastably excited had an average mass of 2.4×10^6 atoms. He studied the dependence of these signals on the electron current and energy (from 40 to 100 eV) and

extrapolated to find a threshold of about 26 eV for this species. The threshold seemed to imply that multiple electron impacts were required, but this assumption was insufficient to explain the experimental ratio of charged to neutral metastables. He argued from experiment that the metastable structure did not consist of widely separated oppositely charged carriers but instead that the initial step in their formation was the creation of an atomic 2^3S excitation in the liquid droplet. This precursor state was expected to evolve to the $a^3\Sigma_u^+$ molecular state as observed in the bulk liquid.⁹⁷ He proposed a model with which he could explain the electron energy dependence of the excitation probability of both charged and neutral metastable clusters.

The next experiments which bear on the question of metastable excitations of helium droplets were by Toennies and collaborators.^{29,37,38,40,96} These experiments were largely mechanical chopper based time-of-flight measurements of a neutral ^4He cluster beam, followed by electron bombardment and mass analysis of the resulting small charged fragments. Their earliest experiments³⁷ showed evidence for the existence of a signal at their off-axis electron multiplier detector which was unaffected by electric fields and apparently traveled at the same velocity as the charged clusters. This was attributed to a neutral electronically excited metastable cluster species. The reason that the signal was seen by the off-axis detector was initially thought to involve light emission as the excited clusters passed in front of the detector. Later^{38,40} it was suggested that detection was via surface ionization when excited clusters struck apertures near the detector, or else via evaporating metastable fragments which could reach the detector directly. The bulk of the information obtained in these experiments came from the study of the bombarding electron energy required for the appearance of the various cluster fragment peaks. One of the clearest but very puzzling results was that the appearance threshold for charged clusters occurred at about 20 eV, which corresponds closely to the threshold for producing the 3S_1 metastable atom, while the clusters identified as metastable did not appear until 26 eV, which is about the ionization threshold for free helium atoms. This indicated that while metastable atomic excitations were being produced in clusters at lower energies, this was not the production path for metastable clusters, which were evidently of a qualitatively different nature. Based on results from studies in bulk helium,⁹⁷ it was suggested that the 3S_1 excitation evolved to a highly vibrating He_2^* molecule which was not trapped in the cluster. On the other hand, if an electron created an ion but did not escape from the cluster and they subsequently recombined, the resulting excitation probably would not have been vibrationally excited and thus be easier to bind stably to the cluster. One other significant source of information was a study of the attenuation of the metastable cluster signal by passing the cluster beam through a scattering box containing low pressure argon gas before ionization. Even though these were very large clusters, the metastable signal was strongly attenuated. It was suggested that the argon atoms were captured by the clusters, and that the impurity then "poisoned" the cluster with respect to its ability to carry a long-lived metastable excitation. The impurity would be quickly Penning ionized

by the excitation and the charged fragments would be ejected and not reach the detector.

A second apparatus described by Martini *et al.*⁹⁸ permitted measurements of the angular distribution of the metastable atoms and clusters created by bombarding a cluster beam by electrons. They could see the expected deflection of the metastably excited atomic component, and could resolve the undeflected metastable excitations associated with large clusters. An observed shift in the appearance threshold for excitation of large clusters compared to that for excitation of the atomic component was attributed to the existence of a density dependent barrier to inject electrons into the conduction band of helium.^{99,100} For large clusters corresponding to supercritical expansions, the barrier was 1.03 eV, which corresponds closely to that measured in the bulk at ordinary density. For smaller clusters formed at higher source temperatures, the shift was smaller. The authors suggested that this indicated a lower density for these clusters.

Optical studies of metastably excited clusters have been carried out by Northby and collaborators.^{101–103} Jiang *et al.*¹⁰¹ formed a beam of long-lived metastably excited clusters which, after a flight time of about 4 ms, passed above an electron multiplier. A background signal was observed which came from metastable molecules which entered the detector attached to clusters and then were spontaneously released. Next an infrared light beam from a tungsten filament was passed through a monochromator and intersected the excited cluster beam above the detector. The release rate increased at certain IR wavelengths, which corresponded to the rotationally broadened $c \leftarrow a$ and $b \leftarrow a$ transitions of the triplet helium molecule ($a^3\Sigma_u^+$) in its lowest vibrational state. Northby *et al.*¹⁰³ improved the resolution and found that both transitions could be quantitatively understood in terms of a highly nonthermal distribution of rotational states of the molecule ($J=3-11$ were missing). One "mystery" peak could not be fit by this assignment. It proved to have a different appearance threshold than the others, which was 1.3 eV above the threshold for producing free atomic 3S_1 excitations. It was suggested that this was a measure of the extra energy required one to leave the bombarding electron in the conduction band^{99,100} so that it could escape after creating the excitation. The threshold for the remaining signal was 0.8 eV higher and indicated that the low vibrational states of the molecule have a different precursor excitation. Kim *et al.*¹⁰² next studied the photodetachment process by using a pulsed laser diode to measure the energy with which the particles were released. They found that particles were emitted with two different characteristic energies, one thermal (≈ 7 K) and one much larger (≈ 0.1 eV). They suggested that the low energy group came from molecules directly detached from the cluster in the excitation event and the energetic group from those which first entered a bound excited state with other particles before decaying. Measurements with a separate temperature tunable laser diode permitted one to resolve two of the rotational lines. They indicated that the peaks were only slightly blueshifted (≈ 0.3 nm) from their vacuum values but were asymmetric with significant high energy tails. This suggested strongly that the molecules reside on the surface.

Henne and Toennies⁹⁴ have studied the energy threshold for metastable production in their high resolution electron bombardment apparatus. They have identified three thresholds: that for creating 3S_1 excitations from bare atoms at 19.82 eV, that for creating 3S_1 excitations near the surface of a cluster (in which the electron's final state is outside the cluster) at 20.07 eV, and that for creating the same excitation in the interior (in which the electron's final state is in the conduction band) at 21.22 eV. The latter threshold was in reasonable agreement with earlier measurements.^{98,102} The difference between the last two thresholds, 1.15 eV, was taken as the energy barrier for injecting electrons into helium. It was in excellent agreement with measurements in bulk helium,^{99,100} which indicates that the density of large clusters is essentially the same as that of the bulk. Their electron attachment measurements indicated that sharp increases were associated with thresholds for creation of various other singlet and triplet excitons in the cluster, which allowed them to study these higher energy neutral excitations as well.

Most recently, Northby and collaborators^{104,105} have carried out detachment spectroscopy measurements with a cavity tunable diode laser which permitted complete resolution of the various rotational lines and the associated structure induced by the interaction of the metastable molecule with the helium surface. All peaks were uniformly asymmetric and blueshifted by 2.7 cm^{-1} from their vacuum values with the exception of $P(1)$ and $R(1)$ at $\approx 2.4\text{ cm}^{-1}$. The latter peak was also split into three resolved components by the surface interaction. The previously noted nonthermal initial state distribution¹⁰³ was confirmed, as was the shift in appearance potential for these lines. They argued that the precursor state is the 2^3P_1 atomic excitation.

3. Negatively charged cluster ions

The existence of negatively charged ^4He clusters was first reported by Gspann.¹⁰⁶ He utilized an in-line time-of-flight method and found that negatively charged clusters with masses greater than 2×10^6 atoms could be detected in his apparatus. The mechanism which binds an electron to such structures is not obvious, however. There is no stable He^- ion, and thus the attraction must be a many particle effect. There is a weak binding of an electron to a planar helium surface which is well known from studies on bulk helium, and it had been predicted that similar surface states should exist on clusters, as long as they were large enough.¹⁰⁷ Gspann interpreted his observations in terms of this exterior electron model.

The next observations concerning negatively charged clusters were reported by Northby and co-workers.^{89,90,108-111} Their first experiments, by Jiang *et al.*,^{89,90} involved the measurement of the energy of large charged clusters, both by an in-line stopping potential method and by a deflection method. They found by the first method that, as for positive clusters, the threshold for the production of negative helium clusters depended on the stagnation conditions only through the stagnation entropy S_0 , and not on P_0 and T_0 separately. The threshold entropy (5.5 kJ/kg K) was somewhat lower than for the positive clusters,

however, and corresponded closely to the entropy at the bulk critical point. This and other experiments showed that negative cluster ions were formed preferentially from larger clusters. In fact, the ion current proved to be an approximately universal function of S_0 . It was suggested further that this was a characteristic of the mass distribution itself, but later studies by Knuth and Henne⁹⁵ indicated that this was an artifact. The deflection method showed that the mass distribution decayed roughly exponentially for large masses, and most importantly, had a threshold size of $N \approx 5 \times 10^5$ below which no negative clusters were seen. While this threshold was about the size predicted for binding a surface electron, further experiments showed that the ions were much more stable in electric fields than expected for a surface electron state.¹¹² Consequently they suggested that the structure was an electron in a bubble state, bound in the interior of the cluster by the polarization force.

The next experiments by Jiang *et al.*¹⁰⁸ involved a deflection energy analyzer combined with a TOF velocity measurement which enabled them to study the threshold behavior in more detail. They found that with a flight time after ionization of ≈ 4 ms, the threshold size of the observed negative clusters was somewhat less than 2×10^5 , but most interesting was the fact that there was a sharp mass peak at threshold whose size, 2×10^5 , was independent of the source conditions. They interpreted this in terms of a model involving the dynamics of the conduction band instability leading to capture and bubble formation. Alternative explanations proposed by others⁹⁴ will be discussed in the following.

Since the binding of an electron in a bubble state to a droplet must be at best metastable, it is important to show that the lifetime of such a state can be longer than the duration of the experiments described above (≈ 4 ms), and that the stability in applied fields should be high enough to explain the observed lifetime⁹⁰ in excess of 0.1 ms in 1000 V/cm. Such a model was proposed by Northby *et al.*,¹⁰⁹ in which it was shown how one could extrapolate measurements of the escape of electrons through a plane surface as a function of field and temperature to the case of liquid droplets. Their conclusion was that the structure should be very stable at the expected cluster temperature, and that it would require a field of several kV/cm to detach the electron on the experimental time scale of a few milliseconds.

It had been recognized from the start^{90,108,109} that if the interior bubble electron model were correct for the structure of the negative ion, the ion should be optically active and readily detectable by electron detachment spectroscopy. Consequently an infrared light beam from a 1 kW tungsten bulb, restricted in wavelength by optical filters, was arranged to cross a negative cluster beam above a channel multiplier which was biased to detect detached electrons. It was seen by Kim *et al.*¹¹⁰ that even with the light turned off, there was a significant spontaneous detachment signal, however. This was consistent with the idea that the structure was metastable, but in retrospect it was certainly too large to be accounted for by the above-described model.¹⁰⁹ When the light was turned on and restricted by a filter to wavelengths longer than 800 nm, the counting rate almost doubled. This was consistent with the idea that IR optical transitions in the

bubble potential could lead to detachment of the electron from the cluster.

A more detailed study of the electron detachment spectroscopy of negative cluster ions was reported by Kim *et al.*¹¹¹ Among the results found using filters were that the spontaneous signal came preferentially from small clusters, while the light induced signal came predominantly from larger ones. Further, it was found that the optically detached electrons were more energetic than the spontaneously released ones. Finally, it was found that while there was some optical signal for wavelengths between 2.5 and 5 μm , the majority of the signal lies between 0.8 and 2.6 μm . An attempt to measure the wavelength dependence in more detail by use of a monochromator indicated that the optical signal had a broad peak at 1.5 μm . These results are all understandable in terms of the electron bubble model and strongly support that identification, but detailed understanding of the peak at 1.5 μm is lacking. It was noted that the transition to the conduction band for an electron confined to a well of radius 18.7 Å and a depth of 0.7 eV would peak at 1.5 μm , but other bound state transitions could equally well play a role.

The next and most recent generation of experiments involving the negative ion were performed by Toennies and collaborators.^{93,94,113,114} The first paper by Fárník *et al.*⁹³ discussed the electron impact charging of both positive and negative ions. Their principal observations concerning negative ions were that the measured size distributions fit a log-normal curve, that in contrast to positive ions the shape of the curve was independent of bombarding electron current, and that this and other observations indicated that in the range from threshold up to about 10^8 atoms the clusters were singly charged. They applied the above-mentioned lifetime model¹⁰⁹ to argue that in this size range, if two electrons are in a single drop one will detach rapidly on experimental time scales.

Undoubtedly the most detailed experiments concerning electron capture by clusters were described in an excellent paper by Henne and Toennies.⁹⁴ Their apparatus contained a well-calibrated high resolution energy source for electron bombardment studies, with provision for detection of positive, negative, and metastably excited clusters. It also contained a deflection energy analyzer and TOF capability which permitted measurement of cluster mass spectra. Their measured negative cluster ion size distributions were clearly exponential for large masses. They found (for a 1 ms flight time after ionization) a threshold size of $N=0.75 \times 10^5$ below which no negative clusters were seen. They also found a mass peak in the threshold region as noted previously.¹⁰⁸ They reported seeing a similar peak in the positive ion distribution, however, and thus they attribute it to a bimodal distribution of the precursor neutral cluster masses. Evidence for two kinds of clusters was found in earlier measurements of cluster velocity distributions,³⁰ in which case the velocity distribution was bimodal as well. Henne and Toennies studied the bombarding electron energy dependence of the charging process and found several peaks, the higher ones correlating well with the simultaneous production of metastable excitations in the cluster. The lowest energy capture thresh-

old of 1.29 ± 0.05 eV was discussed in terms of the energy above the conduction band necessary to form a “proto-bubble,” which has been proposed¹¹⁵ as the precursor to localization of the electron in a bubble state. These experiments¹¹⁶ further supported the structural model of the negative cluster as an electron trapped in a bubble inside a droplet (which the authors characterize as an electron “balloon”!). The size distributions found here have been discussed further in additional papers by Knuth *et al.*^{95,96} (see also references Refs. 49 and 117).

One of the most fascinating studies of negative cluster behavior has been reported recently by Fárník *et al.*^{113,114} They studied¹¹³ the rate of electron detachment from both ^3He and ^4He as a function of both cluster size and applied electric field and found huge differences between the behavior of the two isotopes. The thermal equilibrium model discussed previously¹⁰⁹ would not predict any such qualitative isotopic differences in the stability. They found, for example, that the lifetime for small clusters drops precipitously in the observed threshold region, making it highly likely that these thresholds result from stability considerations and not formation dynamics. They also found that, in the absence of an applied field, $^4\text{He}_N^-$ cluster lifetimes lie in the range 1–200 ms while $^3\text{He}_N^-$ cluster lifetimes were >2 s. In a field, however, in some circumstances $^4\text{He}_N^-$ was the more stable species. They attributed this asymmetry to the idea that in ^4He droplets the electron bubble was unable to thermalize, while in ^3He droplets it could, and they presented a lifetime model based on this hypothesis. Since a charged particle should couple strongly to the surface modes¹¹⁸ (which are the dominant excitations at the expected cluster temperature^{62,119}) it is very hard to understand why they are unable to equilibrate while the more weakly interacting captured impurities clearly can.¹²⁰ There is one case, well known from bulk helium studies,¹²¹ in which charged particles in helium are slow to thermalize, and that is when they are attached to quantized vorticity. Perhaps the origin of this asymmetry lies in a similar effect in ^4He droplets.¹²²

E. Electron bombardment of doped clusters

The earliest experiments that studied the capture of impurities by helium clusters and the ion fragments produced by electron bombardment were described by Scheideman *et al.*,^{67,123} and by Toennies.²⁹ They crossed a room temperature Ne atomic beam with a chopped helium cluster beam (24 bar, 10 K) and observed Ne^+ , Ne_2^+ , Ne_3^+ , NeHe_N^+ , Ne_2He_N^+ , Ne_3He_N^+ , etc., synchronous with the cluster beam fragments, in their mass analyzer. This provided the first unambiguous evidence of stable capture (and multiple capture) of foreign atoms by helium droplets, as well as for clustering of foreign atoms within the droplet. The ease with which many other particles also could be captured in various experimental configurations was also mentioned. They monitored the easily resolved $^{22}\text{Ne}^+$ signal as function of source conditions (P_0, T_0) and found a highly structured dependence. For fixed T_0 they found no observable signal for low pressures. The signal then increased rapidly, passed through a maximum, and then dropped to a much lower value and

leveled out. The maximum in the (P_0, T_0) plane coincided rather closely with the critical isentrope. The initial interpretation was that the $^{22}\text{Ne}^+$ signal was a measure of the capture probability, and that clusters formed in expansions that passed through the critical point were better able to capture foreign atoms than others. As was soon realized,¹²⁴ the process is much more complex, and the overall probability that an impurity ion will appear at the detector also depends strongly on the details of the ion–molecule reactions which lead to the ejection of the impurity fragment. Toennies²⁹ notes, for example, that if one assumes ionization of an impurity in a cluster is the same as if it were free and calculates the sticking coefficient implied by the data, it is $\gg 1$! This clearly implies that the ionization is enhanced by the presence of the cluster. He suggested that ionization or excitation of helium atoms, followed by either Penning ionization of the impurity by metastable excitations or charge transfer from helium ions, could be responsible.

Scheideman *et al.*¹²⁴ made the first major effort to understand the ionization process in detail. They utilized electron bombarded SF_6 doped clusters which produced several SF_n^+ and S_mF_n^+ ion fragments in their detector. Most interestingly, they observed the SF_6^+ ion, which is not normally produced from electron bombarded free SF_6 molecules. By studying the electron energy appearance threshold, they showed that the ionization mechanism corresponded almost entirely to charge transfer from positive holes. While some indications of excitonic Penning or direct ionization processes were found, they were 10^3 times smaller. They argued that the motion of the hole after its creation was initially by a resonant “hole hopping” process first discussed by Atkins.¹²⁵ They estimated that the hole will travel a distance of ≈ 500 Å, corresponding to $> 10^4$ hops, before localizing and forming a He_2^+ ion. If it finds the impurity before this, the charge should transfer and ionize it. The hole and the impurity particle(s) are both driven toward each other and toward the cluster center by polarization forces, making their meeting more likely. They also discussed the ionization process, and looked for an explanation for the matrix, or cage, effect thought to be responsible for the anomalous appearance of SF_6^+ . They suggested that the ionization process in clusters may be particularly “gentle.”

Lewerenz *et al.*⁴³ also provide further discussion of the ionization process as a part of their study of the process of impurity capture by helium clusters. They make and support the assumption that there is negligible fragmentation of the neutral impurity clusters coagulated inside the helium droplets upon ionization by a positive hole.

More recently, Scheideman, Kresin, and Hess¹²⁶ studied the ionization of captured lithium impurities in electron bombarded helium clusters. They determined, by a study of the electron energy threshold for the appearance of Li_n^+ and LiHe^+ , that in contrast to the above-studied species, the ions were formed primarily by Penning ionization by metastable helium atoms. Since alkali atoms are expected to be in surface states, and metastable excitations are also expected to migrate toward the surface (in contrast to holes which are driven toward the center) the difference seemed quite reasonable.

Janda, Callicoatt, and collaborators have studied experimentally and modeled the ionization process for NO ,¹²⁷ Ar ,¹²⁸ Ne ,¹²⁹ and Xe ¹³⁰ in helium clusters whose mean size was varied in the $N \sim 10^3 - 10^4$ range. Their central measurement was of the pickup cell pressure dependence of the various ion fragment currents (including the pure He_2^+ fragment). They found that the above-presented picture is correct in its general form, but significantly different and more complex in its details. The hole hopping takes place over a much shorter distance (fewer hops) than supposed previously, before localizing as a He_2^+ ion and ejecting a He_2^+ fragment. If the impurity is encountered before this, the probability of charge transfer, as well as the resulting fragmentation distribution, depends strongly on the particular impurity. For example, charge exchange to a Ne atom is quite efficient, but fragmentation always leads to NeHe_n^+ and never to Ne^+ , which appears (only weakly) as a fragment of a cluster containing several Ne atoms.¹³¹ They also note¹²⁸ that the “caging” effect indicated by the appearance of the SF_6^+ fragment ion in earlier experiments¹²⁴ may have been an artifact.¹³²

While it is not directly relevant to the formation of positive fragments, it is worth noting that captured impurities also have been shown to affect the ability of a droplet to carry metastable excitations⁴⁰ and easily detached negative charges.¹⁰⁸

F. Photon bombardment of pure clusters

In order for photons to interact with pure clusters, it is necessary for them to have sufficient energy to create a localized electronic excitation of some sort. Given the tightly bound ground state of the helium atom, this implies energies in excess of ≈ 20 eV, and thus synchrotron radiation is appropriate. Such studies have been undertaken at HASYLAB by Möller and collaborators, and at BESSY by Ding, Toennies, and their collaborators. The work carried out by the HASYLAB group^{133–137} involved the study of the fluorescence radiation emitted after excitation by a photon in the 20–30 eV range. The first experiments, reported by Joppien *et al.*,^{133,135} concentrated on the fluorescence excitation spectrum of $^4\text{He}_N$ clusters formed in a nozzle expansion. In an apparatus described by Karnbach *et al.*,¹³⁴ they crossed the synchrotron radiation beamline with a cluster beam and measured the total luminescence as a function of the incident photon energy. This was taken to be identical to the cluster absorption coefficient, and was studied as a function of cluster size. Two rather broad and shifted peaks arising out of the atomic $1s \rightarrow 2p$ and the (forbidden) $1s \rightarrow 2s$ transitions were identified, as well as a broad feature above 23 eV of unclear parentage. They conclude that the normal exciton description, which works in other rare gas solids, appears to fail in the case of helium. In the next series of experiments^{136,138} they studied primarily the spectrum of the visible and IR luminescence that followed cluster excitation by the incident photon. Most emission lines observed correspond exactly to helium atomic and molecular lines measured in the gas phase. Thus they must arise from atoms and molecules which are ejected from clusters as a relatively prompt product of the excitonic relaxation process. As the clusters increased in size,

the molecular lines predominated over the atomic lines, and there was also evidence for nonsharp luminescence from interior states. For higher excitation energy they observed, quite unexpectedly, atomic and molecular lines from the triplet system as well. These could not have been created directly, but evidently when the initial excitonic state permits autoionization, nonradiative recombination processes can lead to system crossing.

The group at BESSY¹³² has studied the photoionization of clusters illuminated by synchrotron radiation as a function of photon energy and cluster size. They measured the mass spectrum of small cluster ions produced by photons whose energy exceeded the bare atom ionization threshold. They found distributions (including magic numbers 7, 10, and 14) which were nearly identical to those obtained by electron bombardment. They also observed the production of small cluster ions (with the exception of bare He⁺) even for energies below threshold. This must follow from excitation of autoionizing excited states. The observed threshold for this process was equal to the energy required to excite the $(3p)^1P$ state of the free atom, which agreed well with expectations. Much larger cluster ions were also observed, and proved to be the principal charged component originating from large neutral clusters. Finally, they were able to show experimentally that the dominant decay process following excitation was fluorescence emission, in agreement with the assumption made by Joppien *et al.*¹³⁵ and noted previously.

V. CONCLUSIONS

While the picture is not totally clear, let me summarize my present understanding of the properties of neutral $^4\text{He}_N$ cluster beams formed through homogeneous nucleation in nozzle expansions. As the source pressure increases or the temperature decreases for a fixed nozzle geometry, the onset of condensation proceeds through the growth of small clusters including $N=2$ as a precursor. The best current information about the onset region comes from the transmission grating interference experiments of Toennies and collaborators.^{54,55} As the source entropy continues to decrease, one may consider that the gas accelerates and cools, with its local single phase state following a line of constant entropy until well after the state crosses the equilibrium coexistence curve into the metastable two phase region. The thermodynamic trajectory in this case crosses the phase boundary from the vapor side. At this point, nucleation and growth of clusters takes place. These clusters can be characterized by their size distribution, and by their velocity distribution, which is very narrow. The velocity is determined by the initial enthalpy in the stagnation volume and by the internal enthalpy of the system at the condensation point. Since the condensation point is determined by several variables including the geometric characteristics of the nozzle, even with identical stagnation conditions there is likely to be significant variation in the velocity and size distributions from one apparatus to another. For the nozzle type currently favored by most groups,¹³⁹ the best experimental information on the size distribution of condensation clusters comes from the particle scattering experiments of the type first described by Lewerenz *et al.*⁴² The best information on velocity is

probably from the TOF measurements described in the papers by Buchenau *et al.*³⁰ Scaling arguments to relate cluster sizes produced in different size nozzles have been presented by Knuth.¹⁴⁰

When the stagnation entropy lies at or below the entropy at the bulk critical point, a new mechanism for cluster formation becomes possible. In this case the thermodynamic trajectory crosses into the two phase region from the liquid side, and it becomes possible to form clusters by fragmentation of the liquid phase.¹⁴¹ After fragmentation, the vapor fraction (fed by evaporation from the fragmentation clusters) continues to expand and eventually another group of clusters are formed by condensation from this component. Whether the properties of these secondary condensation clusters join continuously to those formed in subcritical expansions is an open question. There is a significant region in which the two kinds of clusters coexist. The best experimental information about the velocities in supercritical expansions is again contained in the papers by Buchenau *et al.*³⁰ The most recent experimental information about the size of fragmentation clusters is contained in the papers by Henne and collaborators.^{94,95}

It is clear that there is a sharp distinction between condensation clusters and fragmentation clusters. Under circumstances in which they coexist, they are clearly distinguishable by their average size, and usually their mean velocity. It is also clear, however, that their size ranges overlap. I think it is a valid question whether clusters of the same size, but formed through two very different processes, are in the same internal state by the time they are available for study on the typical experimental time scale of a few milliseconds after formation. At first glance it would seem that they have to be—cooling is certainly by evaporation, and the temperature reached by evaporative cooling is expected to be independent of the initial size and internal state on this time scale.^{62,119,142} The conditions under which they are formed are really quite different, however, and their internal state as they evaporate may remain so. As an example, suppose clusters formed by fragmentation have a different angular momentum distribution than those formed by condensation, so that they are more likely to contain vortex fragments after they cool through the lambda point. It is known that in bulk helium with solid boundaries vortex states are ubiquitous and very difficult to clear out. Perhaps they will persist in evaporatively cooled droplets as well. There is no clear experimental information on this point, to my knowledge, and it would be nice to have some.

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