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The determination of the mean sizes of large He droplets by electron impact induced attenuation

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ABSTRACT

The mean number sizes of large He droplets ($N \lesssim 10^5$ atoms) created in a free jet expansion are measured by attenuating the droplets by the electrons of a mass spectrometer ionizer. Droplets formed at source temperatures of 6, 12, 15 and 20 K and source pressures from 1 to 100 bar are investigated. The resulting values of mean droplet sizes agree well with previous results obtained by an independent method.

1. Introduction

As the only atomic clusters known to be liquid and superfluid, helium clusters have attracted interest from diverse areas of chemical physics [1]. The very weak interaction with other atoms and molecules make He droplets the most gentle and cold cryogenic matrix. They are frequently used to host a variety of closed shell as well as exotic species and are applied in different spectroscopic techniques, such as rotational, vibrational, visible or photoelectron spectroscopies. Most notably, the investigation of the rotational spectra of OCS molecules in He droplets led to the experimental observation of superfluidity of He clusters with sizes down to about 60 atoms [2]. This seminal contribution bridged the gap between applying droplets in spectroscopy and as a model for finite sized quantum many-body research.

The most common way to produce He droplets is through the expansion of the pressurized gas into vacuum. During the ensuing adiabatic expansion the He gas cools down rapidly to very low temperatures of 0.38 K(^{4}He) or 0.15 K(^{3}He) and, if the initial gas density is sufficiently high, condenses to small clusters or droplets seeded in a beam of He atoms. The degree of condensation is controlled by the initial conditions of the source: its temperature and pressure, as well as by the size of the orifice, through which the gas is discharged into vacuum.

Most of the experimental research on He droplets requires a knowledge of the size distributions of the He clusters or droplets produced in the expansion. Several methods have been developed and used to measure cluster and droplet size distributions. For clusters with small numbers of atoms (less than about 100) an elegant approach utilizes their wave nature by diffracting them from the periodic structure of a nanofabricated transmission grating. This approach led to the first unambiguous detection of the very weakly bound He_2 dimer [3] and has been successfully applied to small He clusters [4]. A related method uses similar transmission gratings which are tilted with respect to the incident beam [5]. From the transmission as a function of tilt angle the size distribution is determined.

A different approach has been used to analyze for the size distributions of large He clusters $N > 1000$, which can be considered as droplets of liquid helium. In this method the droplets were deflected out of the beam by collisions with atoms of a secondary atomic beam [6–8]. By measuring the deflection of the droplets out of the initial beam direction the authors were able to determine the masses and thus the sizes of the droplets. It was observed that droplets closely follow a log-normal distribution. The log-normal shape has recently been confirmed by a kinetic nucleation theory [9].The sizes of even larger droplets have been investigated by electron attachment to produce negatively charged droplets [10]. Other simpler approaches have been developed for pulsed droplet beams. By detecting the number of embedded foreign particles either by

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laser induced fluorescence [11] or by electron impact ionization [12,13], the average capture cross-section of droplets could be measured and the mean sizes of the droplets estimated.

The above methods for continuous beams are all relatively complicated and require, for example, the construction of a crossed molecular beam apparatus with a detection system with a high angular resolution. Moreover all except the last method are restricted to droplets with $N \lesssim 10^4$ atoms. Therefore in most of the research publications only the conditions of the droplet source (orifice diameter, gas temperature and pressure) are reported and the resulting droplet sizes are assumed to be equal to those previously published.

In this paper we present another method to detect mean droplet sizes of continuous beams: attenuating them by electron impact ionization. In the apparatus the He droplets cross a beam of energetic electrons. The ionized droplets are deflected out of the beam due to fragmentation and the attenuation of the beam is measured with a subsequent detector equipped with magnet-mass-spectrometer. In this way droplets with sizes up to $N = 10^5$ produced with four different source temperatures and a range of pressures are determined in agreement with previous results [7]. This method, as the methods based on capture, provide mean droplet sizes which rely on the log-normal distribution determined by Lewerenz et al. [6]. It can be relatively easily employed since most He droplet apparatus are usually equipped with a mass spectrometer detector. In addition it only requires the construction of a simple electron gun, which can be calibrated.

2. Experimental conditions

The experiments were carried out on an apparatus shown schematically in Fig. 1 and described in detail elsewhere [15]. In brief, 99.9999% commercially purified He (Praxair) is expanded into a vacuum chamber through a 5 μm orifice. The body of the source and the orifice are cooled using a constant flow cryostat to temperatures ranging form 6 to 20 K, which are known to lead to the formation of large He droplets. As in previous experiments the pressure of He gas is varied between 1 and 100 bar. The He droplets formed in the expansion enter a differential pumping region through a 0.5 mm diamer skimmer (Beam Dynamics) positioned 1 cm downstream from the source. Two successive ionizers of similar design are positioned 1.9 and 2.8 m downstream from the source. The beam is collimated by two vertical 20 μm wide slits separated by 1.1 m. A third 20 μm slit is located 2.6 m downstream from the source between the first and the second ionizers.

Both ionizers consist of a 4.5 cm long ionization region in which an electron beam with currents up to 10 mA crosses the droplet beam at right angles. A sequence of electrostatic lenses for ion focusing and a sector magnet mass analyzer are installed at the exit of the second ionizer. As shown previously the He_2^+ ion is the predominant fragment upon ionization of the droplets [14] and this signal was used to detect the flux of droplet fragments.

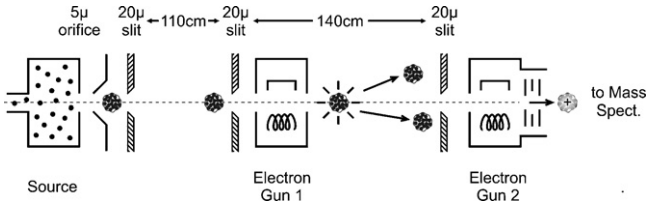

Fig. 1. Schematic diagram of the apparatus. The vertical direction is greatly exaggeratted compared to the horizontal (beam) direction.

When electron current is present in the first ionizer, a fraction of the droplets in the beam is ionized and fragmented. Due to the rebound resulting from the ejection of atoms and neutral or ionized fragments, the remaining major fragment is deflected and can no longer enter the second ionizer. This attenuation depends on the size of the droplet via its electron impact ionization cross-section as well as on the droplet velocity, which determines the ionization probability via the residence time in the ionization region. To confirm, that ionized droplets could not enter the second ionizer, a voltage was applied to deflection plates positioned just after the first ionizer. The presence of the voltage did not alter the recorded signal in the detector, indicating that ionized droplets could not pass through the third collimation slit.

Since the beam velocity depends on the source temperature and pressure and is also different for atoms and droplets due to slippage, a chopper wheel at a distance of 2.32 m upstream from the second ionizer and time counting electronics were used to measure the time-of-flight (TOF) distributions of the droplets. Some of the velocity distributions and droplet beam velocities obtained from the time-of-flight distributions are presented in Fig. 2.

3. Experimental results

In the experiments the droplet signal was first determined from areas under the time-of-flight distributions recorded with the mass spectrometer set to mass 8 amu (He_2^+). The measurements, some of which are plotted in Fig. 2 were carried out for four different nozzle temperatures 6, 12, 15 and 20 K. The pressures between 1 and 100 bar were chosen to produce droplets in the range from 10^3 to 10^5 atoms. For each set of source conditions two measurements were recorded with the electron beam in the first ionizer switched on and off. To confirm the results additional test time-of-flight measurements at mass 4 amu and the total signal (without TOF) at 8 amu were also recorded for some conditions. In all these tests the attenuation of the beam was the same within the errors and thus only the complete set of data at 8 amu is used in the analysis. Fig. 3 summarizes the attenuation data as a function of source pressure for the four source temperatures. The sharp increase in attenuation found in the 6, 12 and 15 K measurements results from the transition of the expansion isentropes from subcritical gas expansions to supercritical liquid expansions [14]. The sharp minimum for the 12 K measurements at about 20 bar is explained by the expansion isentropes passing through the critical point (5.2 K, 2.27 bar) near the orifice and has been observed previously [16].

The attenuation A is calculated as

$$A = 1 - \frac{a_{on}}{a_{off}} \tag{1}$$

where a_{on} and a_{off} are the areas under the time-of-flight peaks with the current of the first ionizer switched on and off, respectively. To extract the average size of the droplets from the attenuation it is necessary to assume a functional form of the cluster size distribution. Lewerenz et al. [6] established that for a wide range of experimental conditions the droplet size population are described by a log-normal distribution:

$$f(N) = \frac{1}{N\delta\sqrt{2\pi}} e^{-((\ln N-\mu)^2/2\delta^2)}, \tag{2}$$

where μ is the natural logarithm of the most probable size and the parameter δ describes the width of the distribution. This experimental observation has been recently confirmed by a kinetic nucleation theory [9].

The experiment provides only one parameter, the attenuation, whereas the log-normal distribution has two parameters. However, in the experiments of Lewerenz et al. [6] it was observed that the full

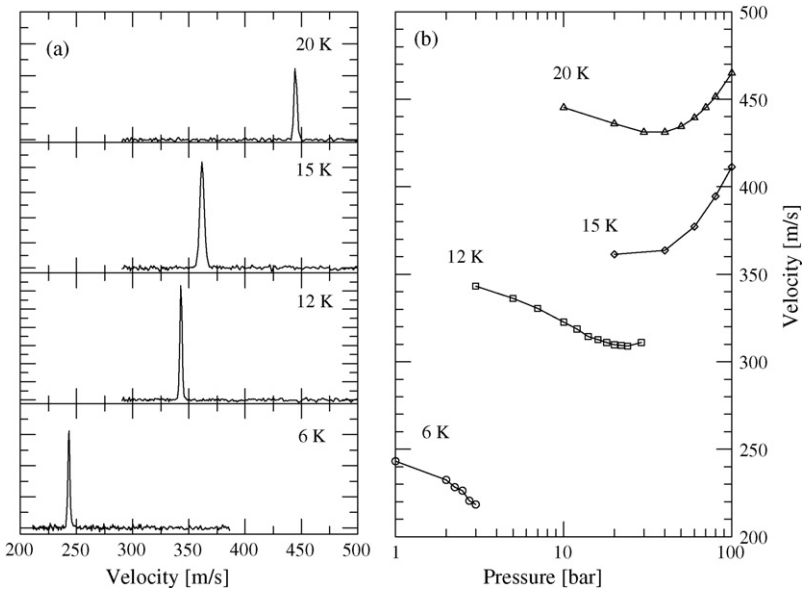

Fig. 2. (a) Some typical velocity distributions of He droplets measured on the mass of the He_2^+ fragment (8 amu) for four source temperatures and pressures: 20 K/10 bar, 15 K/20 bar, 12 K/3 bar, and 6 K/1 bar. (b) Velocities of the cluster determined from the time-of-flight data for the same four temperatures and ranges of pressure used in the experiments.

width at half maximum (FWHM) of the experimental log-normal distribution is always comparable to the mean size of the droplets, which is given by

$$\bar{N} = e^{\mu+(\delta^2/2)}. \tag{3}$$

Here use is made of a special property of the log-normal distribution that for any given mean size $\bar{N}$ there is a maximum value of the FWHM, which is achieved at a specific value of δ approximately equal to $\delta = 0.626$. Hence for the subsequent analysis this value of δ is assumed making the log-normal distribution dependent only on the mean cluster size $\bar{N}$.

When droplets pass through the ionizer, the probability for them to be ionized depends on the droplet ionization cross-section, electron current and velocity of the droplet beam. The latter, together with the length of the ionizer, defines the time during which the droplets are exposed to the electron beam. Since the electrons are moving much faster than the droplets this time and the flux of electrons are then used in Beer's law to determine the droplet ionization probability. For the subsequent calculations the velocity of all droplets in the beam is considered to be the same, which is supported by the narrow velocity distributions presented in Fig. 2 a. According to previous experimental and theoretical research the major ion fragment produced following ionization is the He_2^+ ion [14]. Moreover, for large droplets the relative probability for formation of this ion compared to other ion fragments is essentially constant, independent of the droplet size. Thus the signal detected by the second ionizer is obtained by averaging the ionization probability over the cluster size distribution:

$$a_{off} = nSv\gamma_8 \int_0^\infty (1 - e^{-\sigma(N)j_2(L_2/v)}) f(N)\,\mathrm{d}N, \tag{4}$$

where n is the total concentration of clusters in the beam, S the effective area of the beam, v the velocity of the beam, γ_8 the combined probability of fragmentation to He_2^+ and its detection, $\sigma(N)$ the ionization cross-section for the cluster of size N, j_2 the average electron flux in the second ionizer (current divided by charge and effective area of the electron beam) and finally L_2 is the effective length of the second ionizer.

Obviously, larger droplets have larger ionization cross-sections. Thus when the droplet beam passes through the electron beam of the first ionizer the shape of the size distribution changes and it becomes skewed toward smaller sizes. Therefore the signal detected after the second ionizer, when the electron beam in the first ionizer is turned on, can be expressed as

$$a_{on} = nSv\gamma_8 \int_0^\infty e^{-\sigma(N)j_1(L_1/v)} (1 - e^{-\sigma(N)j_2(L_2/v)}) f(N)\,\mathrm{d}N, \tag{5}$$

where the quantities with subscript "1" refer to the first ionizer and the first exponential factor describes the probability for the droplet of size N to pass the first ionizer unaffected.

Eqs. (4) and (5) can be substituted into Eq. (1) to calculate the beam attenuation and by comparing with the experimental data the mean sizes of the droplets. It can be easily seen that the quantities n, S, and γ_8 cancel in the ratio of Eq. (1). Moreover the analysis is simplified since both ionizers are of the same design with $L_1 = L_2 = 4.5$ cm. Also the same electron current of 6 mA was used in both ionizers. According to the previous investigations with similar

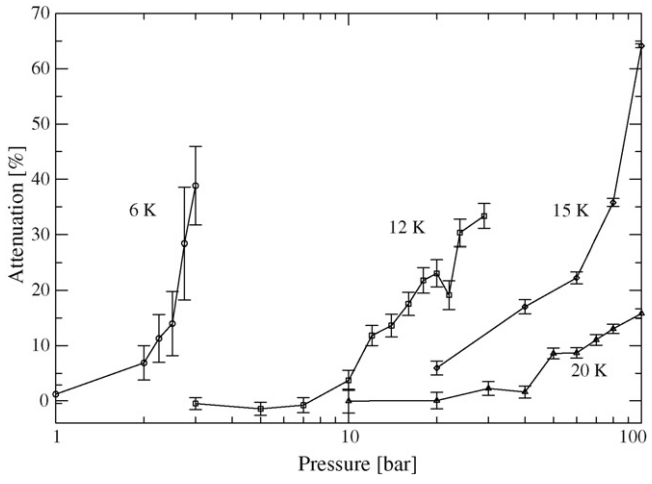

Fig. 3. Attenuation of the droplet signal in the detector due to electron impact ionization of He droplets.

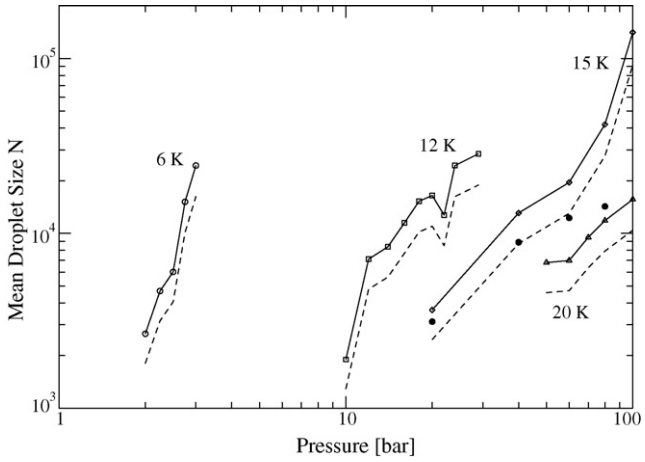

Fig. 4. The open symbols are mean droplet sizes extracted from the attenuation data of Fig. 3 for source temperatures of 6, 12, 15 and 20 K and a range of source pressures. The closed circles are the data points of Harms et al. [7] at 15 K and pressures between 20 and 80 bar. The dashed lines show experimental mean sizes calculated by assuming a larger value of the electron flux, $j = 5.0\,\text{Å}^{-2}\,\text{s}^{-1}$, instead of $j = 3.5\,\text{Å}^{-2}\,\text{s}^{-1}$.

equipment it leads to an electron flux of $j = 3.5\,\text{Å}^{-2}\,\text{s}^{-1}$, which was used in the present analysis.

The last quantity to be defined in Eqs. (4) and (5) is the size dependent cross-section $\sigma(N)$. Following a similar approach for H_2, N_2 and CO_2 clusters [17] the cross-section is assumed to depend on the number of atoms N, the liquid He bulk density $n_{bulk} = 0.0218\,\text{Å}^{-3}$ and the electron impact ionization cross-section of a He atom σ_{el} which at the electron energy of 130 eV used in these experiments is equal to $\sigma_{el} = 0.347\,\text{Å}^2$[18]. Assuming a spherical shape of the droplet and a straight path of the electron through the droplet the ionization cross-section is given by

$$\sigma(N) = 2\pi \int_0^{R(N)} \left(1 - e^{-\sigma_{el} n_{bulk} 2\sqrt{R(N)^2 - r^2}}\right) r\,dr, \qquad (6)$$

where the radius of the droplet is given by $R(N) = \sqrt[3]{((3N)/(4\pi n_{bulk}))}$. For small clusters ($N < 100$) the deviation of Eq. (6) from linear behavior is less than 3 %. For large droplets the cross-section from Eq. (6) is always somewhat less than the geometrical estimate $\pi R(N)^2$.

Using Eqs. (1) and (4)–(6) the attenuation measurements in Fig. 3 were numerically converted to average droplet sizes. Values of the beam attenuation which are within one standard deviation of zero were omitted, since the average cluster size is too small to be determined reliably by the present method. The results are presented as open symbols in Fig. 4 where they are compared with the atom beam deflection method measurements of Harms et al. [7] for a source temperature of 15 K.The mean droplet sizes follow the same trends as the attenuation raw data.

4. Discussion

The comparison with the earlier experiments at 15 K indicates that the new number sizes are larger by about a factor 1.5–3. The major uncertainty in the calculation is in the value of the ionizing electron beam current, which is limited by space charge. It can be shown that the electron flux in the first ionizer has the most prominent effect, while that of the second ionizer does not change the results considerably owing to the cancellation effect in the ratio of Eq. (1).

To investigate this effect the mean droplet sizes were recalculated with an electron flux of $j = 5.0\,\text{Å}^{-2}\,\text{s}^{-1}$, which is chosen to best match the data of Harms et al. [7]. The new results are presented in Fig. 4 as dashed lines. As expected from the exponential factor in Eq. (5) the increase of the electron flux reduces the calculated sizes and the agreement 15 K is significantly improved.

The point at the highest pressure of 80 bar is still larger than the reference point by a factor of 2. However, the deflection method of Ref. [6] is most sensitive for relatively small droplets which are easier to deflect and its accuracy deteriorates for larger droplets, while the method of the present paper is most sensitive to very large droplets with the largest attenuation cross-sections.

Another uncertainty factor, which could influence the results is the density of the He droplets. It is known that the density of the droplet is not constant and decreases towards the surface [7]. The effect of this uncertainty in the cross-section enters into Eqs. (4) and (5) in the same way as the electron flux j and thus the adjusted value of the electron flux will to a certain extent account for this effect.

5. Summary

A new method for determining the mean number sizes $\bar{N}$ of large helium droplets is described. The method involves ionizing the droplets by electron impact and measuring the resulting attenuation of the droplet signal through a narrow slit placed in front of a downstream mass spectrometer detector. A simple theory relates the attenuation to the mean droplet size by assuming a broad log-normal size distribution. The results are in reasonable agreement with previously published experiments at $\bar{N} \lesssim 10^4$ and extend the accessible range to $\bar{N} \lesssim 10^5$. The new method is easily applied to existing apparatus to provide in situ characterization of the droplet beams produced under non-standard conditions. The method is robust against most of the approximations involved. In principle it can easily be adapted to solid or semi-liquid clusters of other substances.

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