Noble Gas Condensation in Controlled-Expansion Beam Sources

by

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Abstract

Over the past several years an investigation into the gasdynamic and nucleation properties of very small Laval nozzles has been undertaken in our laboratory due to their great potential as sources for cluster beams. A series of nozzles designed specifically for helium carrier gas expansions has been tested in our molecular beam apparatus and used to study the condensation of the noble gases, Ar, Kr, and Xe. The goal of producing cluster beams with densities high enough to carry out high energy electron diffraction experiments has been attained for these gases with mean cluster sizes in the range of 100-400 atoms per cluster. The onset of nucleation appears to correlate with the product of nozzle diameter, starting pressure, and atomic potential well depth, i.e., \( p_0 D^2 \sqrt{\kappa} \).

Introduction

It is well known that supersonic nozzles can have their contours designed to control, within limits, the rate of expansion and that they can be very much more effective in nucleating a particular gas than uncontrolled, free-jet sources.

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**An orifice or a converging-only nozzle both of which have their entire supersonic flow regime as free-jets will be defined here as "free-jet" sources. The nozzle sources described in this paper are of the Laval type with supersonic flow in the nozzle before exiting as a free-jet.**
expansions having the same throat diameter.\textsuperscript{1-4} Nozzles made
of varying throat diameter, exit diameter, and nozzle length
have been built and tested. They have been instrumented
so that the following data can be obtained: stagnation pressure
P\textsubscript{0}, and temperature T\textsubscript{0}, nozzle exit static pressure p, pilot pressure measurements \( \frac{p}{p_0} \) near the nozzle exit, and pilot
traverses parallel and normal to the flow direction.

The experimental arrangement is shown in Fig. 1a. The
nozzle source is mounted with gas motion capability and is
shown with a diverging Level-type nozzle installed. If impact
pressure measurements are to be made, the skimmer is removed
and a probe and pressure transducer are mounted so as to sepa-
rate the first and second pumping chambers. Replacement
of the skimmer re-establishes the standard molecular beam
configuration. The cluster beam is crossed by a 40 keV electron beam
for diffraction studies and Debye-Scherrer patterns are taken
with a single-channel, electron-scintillator, photon counting
detection system using phase-sensitive detection and a chopped
molecular beam.

The contours for the nozzles used in this work are shown
in Fig. 1b. The throat diameters vary from 0.05 to 0.1 mm, and
exit diameters range from 2 to 5 mm. The nozzles are diverging
with the minimum diameter at the entrance. The subsonic flow
ahead of the entrance is not important for the nucleation
process. Their contours have been measured and fitted to each
other polynomials as shown in Table 1. Nozzle 6 has the
smallest divergence angle (<1° total included angle) and is
larger than the other nozzles. The noble gas experiments dis-
cussed here were obtained using Nozzles 11, 12 and 13. They
were designed to determine the effect of throat diameter \( D_0 \)
and nozzle contour on their performance as cluster sources.
Nozzles 12 and 13 have the same contour except near the nozzle
entrance. Nozzle 11 diverges more rapidly then 12 and 13 near
the inlet.

Gaseous Measurements

Extensive gaseous measurements using a variety of
gases and gas mixtures reveal that a large fraction of the
nozzle flow lies within the nozzle boundary layer with some
viscous dissipation occurring all the way to the stagnation.\textsuperscript{1-5}
Thus, in order to correctly determine the local Mach number at
any point in the nozzle, one must measure both static and
impact pressures. The only point where both pressures are
measured in this work is at the nozzle exit. The Mach number
is obtained using the so-called Rayleigh supersonic pitot
equation,

\[
\frac{p}{p_0} = \left(\frac{x_0}{x_1}\right)^{1/2} - \left(\frac{x_1}{x_2}\right)^{1/2},
\]

where \( y \) is the local value of the specific heat ratio. The
exit Mach number \( \mathcal{M}_e \) is shown in Fig. 2 for several gas
mixtures, all of which are for 6 mole % of the condensible
species in a helium carrier gas (\( \mathcal{M}_e = 0.06 \)). This Mach number
is seen to increase monotonically with \( p_0 \), to values as high as
10. The three solid curves are for Nozzle 12 with the differ-
ent condensible species. For \( p_0 < 4 \) bar, the Mach numbers are
nearly the same, but increase with molecular mass, i.e., from
Ar to Kr to Xe. Above 4 bar the curves reverse, with Ar having
the highest Mach number for any given \( p_0 \). For Xe, a compar-
tion for the three nozzles, 11-13, is shown. Nozzle 12 gives
the highest Mach number for a given \( p_0 \), and Nozzle 11 (same
throat size but more rapid expansion) is second highest.
Nozzle 13 (same contour as 12 but smaller entrance diameter \( D_0 \))
exhibits the lowest Mach numbers.

With the system arranged in its molecular beam
configuration, beam intensities were measured using an ioniz-
ation gauge (see in Fig. 1). The nozzle-to-skimmer distance,
\( x_0 \), was varied to determine its effect on beam intensity. Pure
argon expansions are shown in Fig. 3. Note that intensity
variations with \( x_0/D_0 \) are not large. There is an interesting
variation in \( I_0 \), the beam intensity proceeding from a down-
stream peak location to a double peak to an upstream peak as \( p_0 \)
is increased. This behavior is similar to some previous free
jet cluster source data.\textsuperscript{6,7} All beam experiments now to be
described were carried out with \( x_0 = 2.5 \) mm. This spacing
involves a value of \( x_0/D_0 \geq 0.5 \) for Nozzle 13, which is optimum
for the high \( p_0 \) beams as seen in Fig. 3. Since the exit
diameter of Nozzles 11-13 are nearly equal, \( x_0/D_0 \geq 0.5 \) for all
of them and their beam intensities are near their maximum
value.
Although level nozzles are much more efficient cluster sources than free-jets for most flows, care must be taken in their design or they can actually produce beam intensities lower than these latter sources. Consider for example the expansion of SF₆ (X₂ = 0.125) through Nozzle 6 shown in Fig. 4. When the SF₆ is expanded in an argon carrier gas, the beam intensity increases drastically near p₂ = 2.5 bar due to clustering. However, for helium carrier gas (same specific heat ratio γ) the beam intensity remains quite low even out to p₂ = 8 bar, as typically seen with free-jet sources. Thus this nozzle is of little use for helium carrier gas, condensation experiments with T₂ near room temperature.

Because a high γ carrier gas is required for condensation of a low γ gas in an adiabatic expansion, and because the level nozzles control the rate of expansion but cannot limit the maximum Mach number in these expansions, He is desirable since it is unlikely to supersaturate and thus will not form condensable/carry gas clusters. The use of pure condensable gas expansions is also an option, provided γ is not too near unity, but such use does not allow the possibilities for controlling the cluster size distribution or temperature that are potentially available through the use of a carrier gas. In addition there is the problem of the high cost of some pure gases such as Xe.

There are, however, a number of problems using He rather than other common carrier gases such as Ar or Ne. For a given nozzle, p₂ and T₂, boundary layer effects are more severe for He due to its higher kinematic viscosity. There is also a problem with the high vacuum diffusion pumps (i.e., for nozzles with Dₙ > 0.1 mm) pressure fluctuations of an order of magnitude or more occurred in the second and third stage pumping chambers when p₂ > 2 bar.) Thus in order to operate at sufficiently high p₂ for cluster beam generation, it is necessary to decrease the nozzle throat size below 0.1 mm. This accelerates the problem of helium boundary layer growth. As a result of these criteria and prior experience with nozzles having long, small divergence inlet, e.g., Nozzle 6, several shorter nozzles that diverge more rapidly have been constructed.

Nucleation

Measured molecular beam intensities for Ne-carried Ar, Kr, and Xe with γ₂ = 0.06 are shown in Fig. 5 for Nozzle 12 and T₂ = 225. As one might expect, condensation occurs in the order Xe, Kr, and Ar as p₂ is increased. All the molecular beam intensity data are given in arbitrary units (but with the same a.u. as those in Figs. 3, 7) with 10 approximately equal to 2 x 10^(-6) atom/(cm²·s) at the electron beam location. Once the beam intensity, I₂ exceeds unity (in a.u.) the beam density is sufficient for electron diffraction measurements. Because all three of these condensable gases are noble species, one is tempted to look for some universal behavior. Thus normalizing to Xe, the three curves are replotted as dashed lines in terms of an abscissa equal to p₂/√k, where k is the interatomic potential well depth κ and k Boltzmann's constant. When plotted in this manner the onset of condensation occurs at the same value of p₂/√k for the three gases.

A plot of these same data as a function of a nondimensionalized or reduced pressure p₂/σ(ν²) or p₂/(C²), where ν is the radius for zero interaction potential and p₂ is the condensable vapor partial pressure, did not unify the onset point.

For a given species and mole fraction, nucleation results from one nozzle to another will now be compared. Results for Ar, X₂ = 0.25, for Nozzles 11-13 are shown in Fig. 6. The solid lines are for the data plotted as a function of p₂. The onset of nucleation occurs first for the nozzles with the two largest diameters. Nozzle 12, with a lower expansion rate than Nozzle 11, exhibits a more rapid growth of the condensate phase after onset since the measured beam intensity beyond onset is due entirely to the condensate phase. As with free-jet cluster sources, these data have also been plotted vs p₂/√k (dashed lines) such that the curve for Nozzle 12 is unchanged. Recall that p₂/√k is proportional to the local number of binary collisions per cent for a given expansion. Here again it is interesting to note that detectable condensation onset occurs.
at a single point on the $p_D$ scale. Note, however, that the
three curves would also converge to a common onset point were
they plotted versus $p_D$, which is proportional to the three-
body collision frequency if this type of collision were re-
quired to form a stable dimer in the initial cluster formation
process. These results, although interesting, are not
universal, as seen in Fig. 7 for expansions with $X_1$ and $X_0 = 0.06$. In this case the onset of nucleation in Nozzle 11
occurs at lower $p_D$ than that of Nozzle 12, and their growth
curves cross over at a higher pressure. When replotted versus
$p_D$ (dashed lines) the results from Nozzles 12 and 13 (which
have the same nozzle contour but different $p_D$) fall nicely on
top of one another, whereas the results from Nozzle 11 move
slightly away. Thus the correlation with binary or tri-
molecular collision frequency is not perfect, but, of course,
these various nozzle expansions do not have flow histories
as universal as those of the free jet expansions.

Electron Diffraction

Electron diffraction patterns have been recorded with our
single channel detection system for all three condensable noble
gases under a variety of conditions and using several nozzles.
An average cluster size can be estimated from the measured
intensities of the diffraction rings in these patterns. Knowing
the density of the condensed phase, the approximate number of
atoms per cluster may then be calculated. Results for $X_0 = 0.06$ are shown in Fig. 6. These results fall in the $g = 100-1000$ atoms per cluster range. There is a correlation of
cluster size $g$ with beam intensity $I_b$, i.e., the higher the beam intensity the greater is the average cluster size. Also,
to obtain a given value for $I_b$ or $g$ in the molecular beam, a
higher $p_D$ and thus higher mass flow rate is required for
Nozzle 13 than for Nozzle 12 and for Nozzle 12 than for Nozzle
11. Therefore, in order to provide a given beam intensity or
cluster size, with the minimum mass flow rate, Nozzle 11 is the
best of the three.

Theoretical models for the structure of noble gas
clusters in this size regime predict the possibility of
icosahedral packing in contrast to the bulk face-centered
cubic (FCC) structure.9,10 The comparisons we have made
between data and cluster models have so far shown better
agreement using icosahedral rather than the bulk structure.
That is to say, the temperature of these clusters is low enough
so that their diffraction patterns reveal a crystalline state
in contrast to that of liquid, and that their structure is
progressively more like icosahedral and less like bulk FCC as
the cluster size is reduced.

Conclusions

We have arrived at the following conclusions with regard
to noble gas clustering in small nozzle nozzles:
1) Noble gases, even when expanded as a small mole-
fraction in helium, readily nucleate.
2) Because of the high kinematic viscosity of helium the
nozzle contour must be carefully designed to balance the
affects of increased boundary layer growth and the requirement
that throat diameter be small enough to avoid pumping problems.
3) There is compelling evidence that a parameter $p_D$
$\alpha/k$ or $p_D R_0^2 \alpha/k$ will provide correlation or scaling with
regard to the onset of nucleation.
4) Cluster beam intensities (actually cluster densities)
high enough to conduct electron diffraction can be attained in
a size range of great interest for study of the structure of the
condensed phase and possible deviations from the bulk-
structure structure.

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References

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1793.


Fig. 1 The experimental arrangements shows the nozzle and stagnation chamber movable in xyz space with either a skimmer-S or a tilt probe and transducer located downstream of the nozzle exit. With the skimmer and collimator C in place the resultant molecular beam is crossed with a 40 keV electron beam which is trapped in a beam trap D. Diffraction patterns are obtained with a detector Det. The nozzle contours are shown in Fig. 1b, with additional details given in Table I.
Fig. 2 Typical exit Mach numbers obtained using Eq. (1) are shown for Nozzle 12 as solid lines for Ar, Kr, and Xe, and as dashed lines for Xe in Nozzles 11 and 13. All expansions begin with $T_o = 773 K$ and $X_o = 0.06$ in a He carrier gas.

Fig. 3 Molecular beam intensities $I_p$ as a function of distance from the nozzle exit to the skimmer. Locations of maximum beam intensity indicated by arrows.
Fig. 4 Molecular beam intensities for SF$_6$ for Nozzle 4 with Ar and He carrier gases.

Fig. 5 Beam intensities as a function of $p_0$ (solid lines) for Nozzle 12 with $X_e = 0.06$ and a He carrier gas. With a scale change to $p_0\ p_0/k$, normalized to Xe, the curves for Ar and Kr move to the dashed lines as indicated by the arrows.
Table I Nozzle Geometry

<table>
<thead>
<tr>
<th>Nozzle Number</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<tr>
<td>4</td>
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<td>0.0099</td>
<td>0.0089</td>
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<td>0.47</td>
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<tr>
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<td>1.356</td>
<td>1.283</td>
</tr>
<tr>
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<td>0.0068</td>
<td>0.0099</td>
<td>0.0055</td>
</tr>
<tr>
<td>a1</td>
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<td>-0.0150</td>
<td>0.0150</td>
<td>-1.162</td>
</tr>
<tr>
<td>a2</td>
<td>0.1468</td>
<td>1.2198</td>
<td>1.6108</td>
<td>2.473</td>
</tr>
<tr>
<td>a3</td>
<td>-0.1136</td>
<td>-4.392</td>
<td>-23.022</td>
<td>-13.250</td>
</tr>
<tr>
<td>a4</td>
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<td>+100.034</td>
<td>-120.048</td>
<td>39.238</td>
</tr>
<tr>
<td>a5</td>
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<td>-341.36</td>
<td>337.06</td>
<td>-63.236</td>
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<tr>
<td>a6</td>
<td>0</td>
<td>375.88</td>
<td>-361.0</td>
<td>59.026</td>
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<tr>
<td>a7</td>
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<td>379.44</td>
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<tr>
<td>a8</td>
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<tr>
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<td>0</td>
<td>129.406</td>
<td>0</td>
</tr>
<tr>
<td>a10</td>
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<td>0</td>
<td>-19.6</td>
<td>0</td>
</tr>
</tbody>
</table>

The best fit polynomial equation, with $b$ and $x$ in cm, is fitted to measured contours:

$$D(x) = \sum_{i=0}^{10} a_i x^i$$

Fig. 6 Beam intensities as a function of $P_o$ (solid lines) and $P_oD_0$ normalized to Nozzle 12 (dashed lines) for Ar, $V_0 = 0.25$ in a He carrier gas.
Fig. 7 Beam intensities as a function of \( p_0 \) (solid lines) and for the ordinate \( p_0 p_0 \) normalized to Nozzle 12 (dashed curves) for Xe, \( X_0 = 0.06 \) in a He carrier gas.

Fig. 8 The average number of atoms per cluster \( \bar{n} \) versus \( p_0 \) for Xe, \( X_0 = 0.06 \) in a He carrier gas for Nozzles 11-13.