

Condensation in Free Jets: Comparison of Rare Gases and Metals

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In view of the recent interest in metal cluster beams obtained from free jet expansions, the paper extends the scaling laws and similarity relations developed for rare gases to metal vapors. The enthalpy of evaporation at 0 K and the density of the solid are used to define for both metals and rare gases, a species-characteristic temperature and length, T_{ch} and r_{ch} . This allows to transform the scaling parameter for condensation of a given gas, $\Gamma = n_0 \cdot d^q \cdot T_0^{(0.25q-1.5)}$, into a reduced scaling parameter Γ^* by replacing n_0 , d and T_0 by their respective reduced terms $n^* = n \cdot r_{\text{ch}}^3$, $d^* = d/r_{\text{ch}}$, and $T^* = T/T_{\text{ch}}$. As shown before for the rare gases, free jets with the same Γ^* are similar with respect to cluster formation. Based on an analysis of existing experimental data in terms of the respective Γ^* , onset of condensation of metals in free jets is correlated by Γ^* too. For $\Gamma^* < 200$ the free jets do not produce clusters, while for $\Gamma^* > 1,000$ clusters exceeding 100 atoms/cluster are being observed.

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Introduction

In 1956 Becker et al. [1] published the first paper on experiments where clusters of H_2 , Ar, and N_2 were produced in free jets of the respective gas expanding out of a nozzle into vacuum. Since that time condensation in such free expansions has been widely used to produce van-der-Waals clusters, i.e. aggregates of rare gases or closed-shell molecules with sizes ranging from dimers up to many thousand monomers [2, 3]. The thermodynamic state of the gas prior to its expansion and the size of the respective nozzle determine whether or not clusters are being produced in the free jet. Cluster formation and growth are favoured by increasing the number density n_0 (or pressure p_0), decreasing the temperature T_0 , and increasing the nozzle diameter d [3, 4]. On a qualitative basis, these dependencies are readily understood, but there is no rigorous theory to predict the resulting cluster size for a given set n_0 , T_0 , and d . However, by accounting for the changes in the kinetic conditions for cluster formation when changing n_0 , T_0 and d , it has been possible to de-

velop scaling laws which correlate flow fields that produce the same clusters [5]. In addition, the concept of corresponding free jets [6] has been confirmed as correlating cluster formation for gases which have the same type of intermolecular potential [4, 7-9].

The last decade has produced an increasing activity in working with clusters from materials like metals or semiconductors, which as solids have to be heated well above their melting point to exhibit vapor pressures high enough for a gasdynamic expansion. Metal cluster beams are of interest not only for basic cluster physics experiments, see e.g. the proceedings of a recent topical conference [10], but for producing high-quality thin films with the cluster ion beam deposition technique as developed by Takagi [11, 12]. In general the experimental results regarding the effects of n_0 , T_0 and d agree with what is known from experiments with van-der-Waals clusters. There is, however, some controversy about the conditions for the onset of massive condensation with cluster sizes in the range beyond 100 atoms/cluster. Using the formalism of classical nucleation

theory it was predicted by Stein [13] that the higher surface tension of metals is the reason that e.g. starting from the saturated state at $p_0 = 133$ Pa, argon is much more favourable than the metal lead. Even addition of argon as carrier gas – which is known to promote the growth of clusters [3, 14] – did not result in significant metal clustering, the cluster size being computed to less than 10 atoms/cluster [15]. These theoretical results unfavourable for the formation of metal clusters have been questioned by others, using again the formalism of classical nucleation theory, but arriving at the opposite result: argon showed a smaller tendency for clustering compared with metal vapors, both starting the expansion from the saturated state at the same p_0 [16–18].

In view of this controversy regarding the predictions of nucleation theory and considering the need for realistic estimates for free jet conditions leading to the formation of metal clusters this paper applies the scalings laws and similarity relations for clustering of different materials to metal vapors. The first part reviews these scaling laws and extends the formalism to metals by introducing a reduced scaling parameter Γ^* based on the values n_0 , T_0 , and d in combination with species-dependent values of characteristic energy and length. The second part evaluates Γ^* for various cluster beam experiments so as to test its validity as a correlating parameter. The final section compares the predictions for cluster size based on the respective values of the reduced scaling parameter with the controversial results of nucleation theory and demonstrates again [3] the non-applicability of nucleation theory to describe cluster formation in free jets.

Scaling Parameter for Condensation

When the gas expands from its initial state n_0 , T_0 out of a nozzle into vacuum, the product $n_0 \cdot d$ is a measure of the “collisionality” of the expansion. It determines the extent of the collision-dominated gas-dynamic regime of the expansion, where the density decrease is coupled with temperature decrease by the equation for an isentropic expansion:

$$n/n_0 = (T/T_0)^{1.5}. \quad (1)$$

The transition to the collisionless free-molecular flow regime and thus the lowest or terminal temperature T_∞ reached in the expansion depends on the scaling parameter Ψ for bimolecular collision processes, i.e. flows with the same value of Ψ , reach the same terminal temperature T_∞ , [5, 19]:

$$\Psi = n_0 \cdot d \cdot T_0^{-1.25}. \quad (2)$$

For simplicity (1) and (2) as well as all subsequent equations are given in the form applicable to monatomic gases with $c_p/c_v = 5/3$ and for circular nozzles. The exact relation between T_∞ and Ψ depends on the type of collision process. For hardsphere atoms for which the product $\lambda \cdot n$ of mean free path and density is independent of temperature the result is [19]

$$T_\infty = K \cdot \Psi^{-0.8} \quad (3)$$

with the constant K depending on the respective gas.

To extend the scaling to *clustering* processes one has to look at cluster formation as a homogeneous gas reaction which consists primarily of *bimolecular collision* processes between atoms and cluster. In addition, however, one has to account for the unimolecular decay reactions of *first order*, i.e. for the spontaneous loss of an atom evaporating from a cluster. This can be shown to yield a new scaling parameter Γ which correlates expansions of a given gas which produce the same clusters [5, 19]:

$$\Gamma = n_0 d^q T_0^{0.25q-1.5}; \quad 0.5 < q \leq 1. \quad (4)$$

The parameter q must be determined experimentally, e.g. from cluster beam measurements where nozzle diameter d is varied at constant T_0 . Note that the upper limit $q=1$ reduces (4) to the bimolecular scaling (2). This confirms the internal consistency of the model for which expansions with only bimolecular reactions are included as a special case.

The scaling parameters Ψ and Γ have been developed and successfully used for free jets of rare gases. However the kinetic analysis which resulted in these scaling parameters is actually not restricted to this class of gases, but applies equally to e.g. metal vapors for which the adiabatic cooling in the free jet and the cluster formation are again the results of binary collisions and unimolecular decay.

A more complex problem is the correlation of experiments with *different* gases. By combining the thermodynamic similarity of gases in corresponding states with the gasdynamic similarity of expansions with the same Knudsen- or Reynoldsnumber one arrives at the concept of corresponding jets. It is valid for the rare gases and has been used and verified experimentally ever since the first results correlating the cluster size in rare gas cluster beams [4]. To extend this similarity concept from rare gases to *metal vapors* is not a simple procedure. Even groups of “similar” metals like the alkalis do not show the kind of similarity or reducibility of the thermal and caloric properties which is characteristic for the rare gases. For example, the vapor pressure p_v for the liquid phase of the rare gases can be

expressed in reduced form [20]:

$$\ln(p_v/p_c) = 5.3 (1 - T_c/T). \quad (5)$$

For the alkalis the corresponding reduced vapor pressure equation results in different constants: The factor 5.3 changes from a low of 4 for Cs to a high of 5.1 for Li [21]. This demonstrates that there is no simple similarity among the alkalis themselves, not to speak of similarity between the alkalis and the rare gases. This can be traced back to the different nature of the metallic bond in the condensed phases, compared to the pairwise additive interaction potentials of the atoms in a rare gas crystal. Nevertheless, for lack of anything better one can try to exploit the remaining traces of similarity [21]. This brings up the more practical problem of defining characteristic values for each substance so that the condensation parameter can be made nondimensional. In (5) the pressure and temperature of the respective critical point were used, whereas [4] used the constants ε and σ of the interatomic potential to obtain a characteristic temperature ε/k , with k being the Boltzmann constant, and a characteristic length σ . Both procedures are not available for correlating rare gases with metals, because neither the critical point coordinates nor the potential constants are known for all substances. Thus an alternative set of characteristics is used:

$$r_{\text{ch}} = (m/\rho)^{1/3}, \quad (6)$$

$$T_{\text{ch}} = \Delta h_0^0/k, \quad (7)$$

where m is the atomic mass, ρ the density of the solid, and Δh_0^0 the sublimation enthalpy per atom at 0 K. The same characteristic variables have been used by Allen [22] in his correlation of surface tension data for metals.

This choice of r_{ch} and T_{ch} is, for the rare gases, consistent with the principle of corresponding states which postulates that the density scales as m/σ^3 , thus making r_{ch} a multiple of σ , and that the enthalpy or heat of condensation scales as ε , thus making T_{ch} a multiple of ε/k . Taking argon as example, where $\varepsilon/k = 120$ K and $\sigma = 0.34$ nm were used previously [4], and for which $m = 6.63 \cdot 10^{-26}$ kg, $\rho = 1,707$ kg/m³, and $\Delta H_0^0 = 7.7$ kJ/mol, one obtains:

Argon:

$$r_{\text{ch}} = 0.339 \text{ nm} = 0.995 \cdot \sigma \quad (8)$$

$$T_{\text{ch}} = 927 \text{ K} = 7.72 \cdot \varepsilon/k.$$

The units of length and temperature together define the characteristic pressure as

$$p_{\text{ch}} = k \cdot T_{\text{ch}}/r_{\text{ch}}^3 \quad (9)$$

which for argon is $p_{\text{ch}} = 329$ MPa.

Using these characteristic units the scaling parameters can be rewritten in nondimensional form by introducing the reduced variables:

$$\begin{aligned} n_0^* &= n_0 r_{\text{ch}}^3; \\ T_0^* &= T_0/T_{\text{ch}} \quad d^* = d/r_{\text{ch}} \quad p^* = p/p_{\text{ch}}. \end{aligned} \quad (10)$$

The final result from combining (2), (4), and (10) is

$$\Psi^* = \Psi/\Psi_{\text{ch}} = \Psi \cdot r_{\text{ch}}^2 \cdot T_{\text{ch}}^{1.25}, \quad (11)$$

$$\Gamma^* = \Gamma/\Gamma_{\text{ch}} = \Gamma \cdot r_{\text{ch}}^{3-q} \cdot T_{\text{ch}}^{(1.5-0.25q)}. \quad (12)$$

To determine the reduced scaling parameters Ψ^* and Γ^* for a particular free jet experiment, Table 1 gives the relevant characteristic variables for a selection of materials, both rare gases and metals. The use of these reduced scaling parameters shall be demonstrated by estimating the terminal temperatures T_∞ . Here (3) can be written in nondimensional form, using the constant K for Ar given in [19] and Ψ_{ch} from Table 1 with the result:

$$T_\infty^* = 0.6 \cdot (\Psi^*)^{-0.8}. \quad (13)$$

Note that (13) assumes hard-sphere type collisions, with more refined models giving a somewhat lower temperature. Evaluating (13) for the experimental conditions of an expansion of silver with $p_0 = 1,333$ Pa, $T_0 = 1,810$ K, and $d = 2$ mm gives $\Psi^* = 277$ and thus $T_\infty = 230$ K. This compares well with the temperature of 190 K as measured by Yamada et al. [16, 18].

The characteristic pressures and temperatures of Table 1 have been used to obtain the reduced vapor pressure curve. Figure 1 shows the usual $\ln p_v^*$ vs. $1/T^*$ diagram for argon together with five metals. The temperature range covered is $21 \leq 1/T^* \leq 33$, with the corresponding values for argon from 44–28 K and for silver from 1,630 to 1,037 K. The reduced vapor pressures show a fair agreement, with the metal curves being nearly parallel and less steep compared with argon. A better fit could be achieved by adjusting r_{ch} , e.g. an increase by 25% would decrease p^* by a factor of 2. Such refinements, however, are not appropriate in view of the other approximations and uncertainties. Note e.g. that for the temperatures shown the condensed phase is *liquid* for argon, but *solid* for all metals. The reduced melting point temperature varies around 0.03 for the metals, while it is $T_{\text{melt}}^* = 0.09$ for the rare gases. This big difference has been used by Gspann [24] to predict that metal clusters in free jets are liquid, while rare gas clusters are known to

Table 1. Characteristic properties of gases and metal vapors. T_{ch} is obtained from (7) using the data of [23]

Element	$r_{ch}/(10^{-12} \text{ m})$	$T_{ch}/(10^3 \text{ K})$	$p_{ch}/(10^9 \text{ Pa})$	$\Psi_{ch}/(10^{14} \text{ m}^{-2} \text{ K}^{-1.25})$	$\Gamma_{ch}/(10^{14} \text{ m}^{-2.15} \text{ K}^{-1.29})$
Ar	339	0.927	0.329	17,0	347.0
Kr	352	1.285	0.406	10,5	210.0
Na	340	13.0	4.57	0,62	11.5
K	422	10.9	2.00	0,50	9.1
Cs	490	9.5	1.1	0.44	7.8
Cu	227	40.6	47.6	0.33	6.3
Ag	257	34.2	27.7	0.32	6.0
Au	259	44.2	36.0	0.24	4.3
Al	255	37.5	31.2	0.29	5.5
Ga	270	32.5	22.9	0.31	5.8
In	296	28.6	15.1	0.30	5.6
Ge	283	45.4	27.7	0.19	3.4
Pb	312	23.7	10.8	0.35	6.4
Fe	227	48.5	56.8	0.27	5.0
Ni	222	40.6	51.2	0.35	6.6
Zn	248	15.7	14.2	0.93	17.8
Cd	278	13.5	8.65	0.76	16.9
Hg	286	7.77	4.57	1.67	32.4

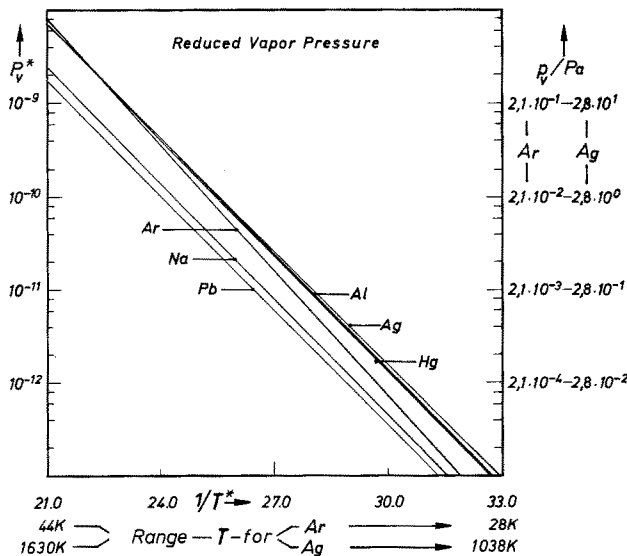


Fig. 1. Reduced vapor pressure as function of inverse reduced temperature for argon and the metals Al, Ag, Hg, Na and Pb, based on the data of [23] and the characteristic pressures p_{ch} and temperatures T_{ch} given in Table 1. For comparison, for Ar and Ag the absolute values of $p_v = p_v^* \cdot p_{ch}$ and $T = T^* \cdot T_{ch}$ are listed in the figure

be solid. This prediction is a consequence of assuming that clusters of a given size have the same reduced temperature, and that this reduced temperature is the same for metals and for rare gases.

For applying the scaling parameter Γ one has to decide on the value of q within its limits of $0.5 < q \leq 1$. First signs of condensation affecting the terminal temperature reached in the free jet became noticeable under conditions correlated by $q=1$ [25]. For another set of experiments by Habets [8, 9] where onset was defined from the measured dimer concentration and the measured change in the flow velocity of argon free jets, the value $q=0.88 \pm 0.05$ was obtained. For more massive condensation, with cluster size between 500 and 2,000 atoms/cluster, the results were represented by $q=0.8$ [4, 5]. On the basis of these experimental results the value chosen was $q=0.85$. This choice of $q \neq 1$ produces different numbers for Ψ_{ch} and Γ_{ch} and of course for the respective reduced quantities. The relative changes, however, are quite similar, e.g. the values in Table 1 differ by a factor of 90 for Ψ_{ch} and 102 for Γ_{ch} . Note that the exact value of q is not very critical when comparing different gases, as long as the reduced nozzle diameters and reduced source temperatures are of the same order of magnitude. Again it should be stressed that one can not predict that metal and rare gas clustering are correlated by the same scaling parameter Γ^* . Whether this parameter is useful in correlating and predicting clustering of rare gases and metals can only be tested by experiments.

A first attempt to correlate clustering in gases and metal vapors has been made by Kuiper et al.

[26]. Using what they called an “intuitive approach” they compared clustering in free jets using as correlating parameter the term

$$\Phi = p_0 \cdot d \cdot (T_B/T_0)^{2.5}. \quad (14)$$

Neglecting for the moment that the boiling temperature T_B is not the best choice for a species-characteristic temperature [20], this term is a mixture of reduced and non-reduced free jet variables. To make it nondimensional a factor r_{ch}^2/kT_B should be added. This shows that aside from the effects of r_{ch} – which are not very pronounced, see Table 1 – this term Φ overestimates the effect of the characteristic temperature T_B . Note that for a given gas (14) corresponds to $q=1$, for constant T_0 , and $q=0$, for constant d . This violates the similarity characteristics of free jets [5]. Thus neither the p_0 , T_0 , d dependence of condensation of a given gas, nor the results of different gases should be expected to be fully correlated by (14).

Comparison with Experiments

A summary of the experimental data to be discussed in this section is presented as Table 2. For each cluster beam experiment it lists the respective set of d , T_0 and both n_0 and p_0 . In addition the reduced source temperature T_0^* and finally both scaling parameters Ψ^* and Γ^* are evaluated. The discussion

will concentrate on the last two columns where the value of Γ^* and the observed clustering have to be compared. The rather vague statements in the column “comments” reflect the difficulty of assigning a quantitative datum to the “cluster quality” of a beam experiment. This is due to the many factors that can influence the cluster distribution in the beam and its determination by the diagnostic method chosen: mass separation, skimmer interference, preferential scattering, ion fragmentation, ionization cross section, detection probability. These problems are, however, less important when concentrating on experiments in the region of onset of condensation.

The first group of experiments no. 1–6 Table 2 describes the experience with rare gases, taking argon as the standard substance. Arranged in order of increasing Γ^* the first defines the conditions which resulted, for $T_0=300$ K, in the lowest terminal temperature prior to onset of condensation. The second corresponds to the conditions which Habets used as onset point. The third line gives the data for which Becker et al. first observed clustering of argon at low source temperatures, for which the onset of clustering becomes detectable as a distorted double-peaked time-of-flight signal, the most probable velocity of the clusters being somewhat slower compared to the monomers. Experiment no. 4 by Kuiper et al. as well as our own data no. 5 and 6 determined cluster size with a retarding field analyzer. To summarize these data there is no evidence for cluster formation for

Table 2. Summary of experiments with clusters in free jets

No	Ref.	Gas	d/mm	T_0 /K	p_0 /133 Pa	n_0 /m ⁻³	T_0^*	Ψ^*	Γ^*	Comments
1	[25]	Ar	0.15	300	567	$1.82 \cdot 10^{25}$	0.32	1300	191	highest Machnumber-no cluster
2	[8]	Ar	0,1	300	1200	$3.9 \cdot 10^{25}$	0.32	1835	289	onset of condensation
3	[1]	Ar	0.3	187	203	$1.0 \cdot 10^{25}$	0.20	2700	347	distorted TOF-signal
4	[26]	Ar	0.4	300	1900	$6.1 \cdot 10^{25}$	0.32	11000	1470	mean size 300 at./cluster
5	[4]	Ar	0.5	223	1000	$4.3 \cdot 10^{25}$	0.32	15000	1836	100 at./cluster
6	[4]	Ar	1.5	96	157	$1.6 \cdot 10^{25}$	0.10	46000	5144	1000 at./cluster
7	[27]	Na	0.025	1100	440	$3.8 \cdot 10^{24}$	0.08	243	49	predominantly Na, Na ₂
8	[28]	Na	0.12	980	125	$1.2 \cdot 10^{24}$	0.08	433	68	predominantly Na, Na ₂
9	[14]	Na	0.2	1073	350	$3.1 \cdot 10^{24}$	0.08	1660	242	max. Na ₂ , up to Na ₈
10	[26]	Ag	0.4	1773	7	$3.8 \cdot 10^{22}$	0.05	41	5	no clusters obs.
11	[29]	Ag	1.0	1700	3	$1.7 \cdot 10^{22}$	0.05	45	5	$500 - 10^3$ at./cluster (?)
12	[18]	Ag	2.0	1820	10	$5.3 \cdot 10^{22}$	0.05	277	28	$500 - 10^3$ at./cluster (?)
13	[30]	Pb	0.5	1523	30	$1.9 \cdot 10^{23}$	0.06	285	37	mean size 1.05 at./cluster
14	[30]	Pb	0.5	1623	60	$3.6 \cdot 10^{23}$	0.07	516	65	mean size 1.2 at./cluster
15	[28]	Hg	0.12	620	760	$1.2 \cdot 10^{25}$	0.08	2800	437	max. Hg ₁ , up to Hg ₂₅
16	[31]	Cu	0.6	2500	100	$3.9 \cdot 10^{23}$	0.06	393	47	traces of trimers
17	[32]	Al	2.0	1823	2	$1.1 \cdot 10^{22}$	0.05	60	6	high-quality thin films

$\Gamma^* < 200$, while clusters in excess of 100 are found beyond $\Gamma^* > 1,000$.

Three experiments with sodium clustering are selected for Table 1. Experiment no. 7 dates back to 1967. It used vapor pressures up to 10^5 Pa and did not present mass spectra for a specific set of p_0 , T_0 . Only the qualitative features of the mass spectra obtained with a sector-field spectrometer are presented in the paper with the statement "the beam is predominantly monatomic and diatomic, with smaller concentrations of Na_3 , Na_4 , Na_5 ..., etc. Clusters up to Na_8 have been detected". With using not the highest pressure for Table 2, this experiment is considered as being below the level of onset of condensation. Note that for equilibrium the sodium dimer concentration for that experiment is about 10% [23]. No. 8 does present mass spectra, obtained with 9 eV electrons and with photoionization. Both methods produced similar spectra for the conditions listed, with the dimer signal exceeding that of the monomer, but bigger clusters having only marginal intensities. This is similar to the next experiment no. 9, which again showed the dimer as the biggest ion peak.

For silver, again three experiments are listed. No. 10 is from a paper which usually used silver vapor seeded with Ar or He as carrier gas, thereby producing clusters of about 30 at./cluster. Without carrier gas, they did not find clusters within their range of n_0 , T_0 and d . This is the basis for classifying this set as yielding "no clusters". Experiments no. 11 and 12, however, with still very low Γ^* values of 5 and 28, are reported as producing clusters in the range of 500–1,000 clusters. No quantitative data on cluster intensity relative to monomers are given, the cluster size being estimated from energy spectra and being apparently insensitive to changes of d and T_0 . Note that for no. 12 additional information on beam velocity and temperature and its dependence on nozzle diameter is fully consistent with what one would expect for a high-intensity uncondensed silver nozzle beam, see e.g. the estimate for T_∞ made in the discussion of (13).

The experiments no. 13 and 14 with lead showed some small clusters, measured with a TOF mass spectrometer, which were analysed in terms of a mean cluster size. This paper studied not only simple sonic nozzles, for which the data are listed in the table, but used converging-diverging supersonic nozzles and channel-type nozzles. As expected and confirmed with rare gases [4, 6] the addition of a diverging section to slow down the expansion rate did increase somewhat the cluster size. There was, however, almost no difference between channel type and sonic nozzle. This result can be taken as con-

sistent with the model that clustering occurs primarily in the supersonic part of the flow, the subsonic flow geometry being of minor importance, as long as severe boundary layer effects are avoided.

The data for Hg, no. 15, are described in the paper as a sudden change in the spectrum, with clusters up to Hg_{25} being detected. The relative intensities of the clusters were still low, around 0.3% for the range from Hg_2 to Hg_{12} . Compared with $\Gamma^* = 437$ this result is in good agreement with what was observed for Ar.

The only Cu experiment no. 16 is from a spectroscopic investigation of a nozzle beam containing some dimers. Certain features in the dimer spectrum were explained as being perhaps due to larger clusters, e.g. trimers. For the value of Ψ^* one can estimate from (13) $T_\infty = 205$ K. The rotational temperature of the dimers was measured to be 800 K, which is not unreasonable, because dimers will be formed in excited states, and are not in thermal equilibrium with the monomers.

The last set of data is included as typical for conditions of the Kyoto group when producing Al beams for what is referred as cluster beam deposition. While this technique yields thin films with unique properties, the respective value of $\Gamma^* = 6$ is not high enough to expect free-jet clustering, compared with the experience with other metals.

To summarize the results of these experiments one can conclude that the classification

$\Gamma^* < 200$	no clustering observed
$200 < \Gamma^* < 1,000$	transition from flow without condensation to flow with formation of clusters
$1,000 < \Gamma^*$	massive condensation, cluster size exceeding 100 atoms/cluster

holds not only for argon, but for the metal vapor expansions, too.

The experiments of the Kyoto group, no. 11, 12, and 17, do not fit into this scheme. While there is no doubt as to the surfaces and their properties and to the detection of clusters by several methods more additional information is required to arrive at a proper conclusion. The fact that measured speed and temperature in the silver free jets is in agreement with what one expects for uncondensed supersonic beams, including the effect of change in nozzle diameter and temperature/pressure, does not allow to expect massive condensation under these conditions. Perhaps the clusters observed result from impurities acting as centers for heterogeneous nucleation with the resulting clusters being of such small concentration that the accompanying release of latent heat

of condensation does not affect the energy balance of the jet. Any speculation however as to what caused the clusters observed should be postponed in order to first provide more data to characterize the experimental situation of production and detection of these clusters.

The reduced scaling parameter Ψ^* for *bimolecular* processes has been listed in Table 2, too. Since it equals Γ^* for the choice $q=1$, it allows to estimate the effect of q on the value of Γ : Both Ψ^* and Γ^* show the same qualitative trend, with the absolute numbers differing by about one order of magnitude, but the relative changes being quite similar: the argon data no. 1–6 show an increase of Ψ^* by a factor of 35, while Γ^* increases by a factor of 27. As discussed above these small differences in the variations of Ψ^* and Γ^* are a direct consequence of the small range of reduced nozzle diameter d^* and source temperature T_0^* .

Comments on the Results of Nucleation Theory for Cluster Formation

The status of condensation theory with respect to the prediction of cluster formation in free jets has been discussed in previous papers [3, 19]. The classical liquid-drop theory and its modifications are still being debated, with the proper accounting of the eigenstates of the cluster being one of the stumbling-blocks. Its application to condensation in nozzle flows, pioneered by Oswatitsch [33] in 1942 gained momentum when modern computers reduced the time for doing the calculations from “one to two hours for a trained expert for one step of 1/2 mm” [33] to almost unmeasurably short times. What did not change, however, are some basic problems with the physical model which were already mentioned by Oswatitsch:

- the nucleation rate used was developed for a steady state. It should be applied only to slow expansions
- the results depend very much on surface tension and the details of the growth law (mass and energy transfer coefficients)
- these data and their variation with cluster diameter are not well known for the low temperatures of the condensing gas
- small cluster of e.g. 30 at./cluster can no longer be described by theories assuming properties of a continuum.

Another inconsistency of the model, the need of a Maxwell demon to replace supercritical clusters by the respective number of monomers to maintain

conditions of constant pressure could now be resolved by noting that for a free jet condensation takes place under isochoric [34], not isobaric conditions. However, this improvement has not yet been incorporated into the computer programs.

Despite these limitations the controversial results of applying nucleation theory to predict clustering in metal vapor jets as compared to rare gases require a discussion of the respective papers [13, 15–18].

They all used the same equations to describe the nucleation process, with the nucleation rate J , the number of critical size nuclei formed per unit time and volume given as

$$J = n^2 \cdot v \cdot (2\gamma/\pi \cdot m)^{1/2} \exp(-\Delta G/kT) \quad (15)$$

with

$$\begin{aligned} \Delta G/kT &= (16\pi/3) \cdot (\gamma v^{2/3}/kT)^3 (\ln S)^{-2} \\ n &= p/kT = \text{number density} \\ v &= \text{volume per atom of condensed phase} \\ \gamma &= \text{surface tension} \\ S &= p/p_v = \text{saturation ratio.} \end{aligned}$$

The radius of the critical nucleus is

$$r_{\text{crit}} = (2\gamma v)/(kT \cdot \ln S) \quad (16)$$

and the number of atoms in the critical size nucleus is

$$N_{\text{crit}} = (4\pi/3) \cdot r_{\text{crit}}^3/v. \quad (17)$$

As expressed by these equations (15–17), the nucleation rate and the size of the critical nuclei are functions of the thermodynamic state p , T of the respective element. To demonstrate the dependence of J and N_{crit} upon the thermodynamic state and the material properties, Table 3 lists data for argon at $T = 40$ K and saturation ratios $S = 10^2$, 10^3 and 10^4 . These p , T states correspond to isentropic expansions which cross the vapor pressure curve between 67 and 16,000 Pa (0.5 and 120 torr), which includes the conditions of the previous analysis [13, 15–18]. For a source temperature of 300 K, the respective source pressures vary between 5.1 and 510 kPa (38 and 3,800 torr). As the data of Table 3 show, increasing S and therefore p by a factor 100 decreases N_{crit} by about a factor 10, but increases nucleation rate by a factor between $10^{4.3}$ and $10^{1.7}$, depending on the assumed value of γ . Similarly, decreasing the surface tension from 0.025 to 0.0174 N/m decreases N_{crit} by a factor 3 and increases J by a factor between $10^{3.4}$ and 10^8 , depending on the assumed value of S . This different sensitivity of J to the same relative change in S or γ reflects the relative change of the Boltzmann factor $\exp(-\Delta G/kT)$, which is the

Table 3. Data for nucleation of argon at $T=40$ K, $p_v=0.331$ Pa. Listed are the values of N_{crit} , $\Delta G/kT$, and nucleation rate J (15)–(17) for three different saturation ratios S , corresponding to gas pressures p of 33.1, 331, and 3,310 Pa, and three different values of surface tension $\gamma \cdot v = 4 \cdot 10^{-29} \text{ m}^3$

$S = p/p_v$	10 ²	10 ³	10 ⁴	10 ²	10 ³	10 ⁴	10 ²	10 ³	10 ⁴
$\gamma/(N/m)$	N_{crit}	N_{crit}	N_{crit}	$\Delta G/kT$	$\Delta G/kT$	$\Delta G/kT$	$J/(m^{-3} s^{-1})$	$J/(m^{-3} s^{-1})$	$J/(m^{-3} s^{-1})$
0.0250	51	15	6	117	52	29	$7.0 \cdot 10^{-23}$	$1.5 \cdot 10^8$	$1.2 \cdot 10^{20}$
0.0200	26	7	3	60	27	15	$4.8 \cdot 10^2$	$1.6 \cdot 10^{19}$	$1.9 \cdot 10^{26}$
0.0174	17	5	2	40	18	10	$3.7 \cdot 10^{11}$	$1.3 \cdot 10^{23}$	$2.9 \cdot 10^{28}$

greater, the greater the absolute value of the exponent.

These data demonstrate the extreme sensitivity of J upon the value of surface tension γ . The three values assigned to γ have been used in [18] (0.025), [17] (0.02) and [35] (0.0174). References [17] and [35] both assumed γ to be independent of temperature, while [18] included an increase of γ with decreasing T . In addition [16] included a dependence of γ upon the radius of the nucleus, which explains the marked differences in J reported in [16] and [18]. However, considering the rather small size of critical nuclei between 50 and 2 atoms per cluster the range of conditions listed in Table 3 is always outside the regime, for which the classical liquid drop theory may be valid, and nucleation should be treated by an atomistic approach [35].

Being aware of this general limitation as far as quantitative answers from nucleation theory are concerned, it is of course possible to evaluate the qualitative trends of nucleation, when comparing different gases. It is not correct to exclude metal vapor nucleation on the basis of the high surface tension of liquid metals: As pointed out before [17, 18] the exponential factor dominating the nucleation rate (15) depends on $(\gamma/T)^3$, and the increase of γ for the metals is paralleled by a compensating increase of T . While this has been evaluated for specific conditions of pressure, temperature and saturation ratio [16–18], a more general result is obtained using the expression for γ in the form of Eötvös' law [22]:

$$\gamma \cdot v^{2/3} = c \cdot (T_c - T). \quad (18)$$

This can be combined with the second factor determining $\Delta G/kT$ in (15) with the result:

$$(\gamma \cdot v^{2/3}/kT)^3 = (c/k)^3 \cdot \{(T_c/T) - 1\}^3. \quad (19)$$

Thus, for a given saturation S , $\Delta G/kT$ depends only on the reduced temperature T_c/T and on the Eötvös

constant. While similar fluids have the same constant c , metals and rare gases are quite dissimilar, the c -value for metals is only 1/3 of the rare-gas value [22]. Thus, at corresponding temperatures $T_c/T = \text{const.}$, metals have a lower $\Delta G/kT$ and therefore a higher nucleation rate J . If however the comparison is made for the same saturated vapor pressure [15–18], this formal advantage of metal vapors is compensated by the fact, that their reduced temperature is lower – which increases $\Delta G/kT$. The actual results of evaluating J for metal vapor expansions depends again on the details of the data assumed for γ , v , and p_v , and different results simply reflect different input data. Note that the periodic group II metals Hg, Cd, Zn and Mg differ from all other metals, they have a higher c -value which has been explained by a different structure of the liquid [22].

While a qualitative comparison of nucleation may be based on the respective nucleation rates J – provided that consistent data for γ , v and p_v are available! –, one should not correlate the onset of condensation with J reaching a critical value. E.g. Fig. 3 of [13] postulates J between $10^{22} - 10^{24} \text{ m}^{-3} \text{ s}^{-1}$ as “practical boundary between nucleation onset and no nucleation for free jets with He as carrier gas”. In [17] this is repeated as “clusters become measurable for $J > 10^{22} \text{ m}^{-3} \text{ s}^{-1}$ ”. Both statements are at best true for a given flow field geometry, characterized e.g. by the diameter of the equivalent sonic nozzle d_{eq} [3]. Note that within the framework of nucleation theory J depends only on the thermodynamic state, while all cluster beam experiments demonstrate the need to account for the kinetic conditions of the growth process by including the diameter d into the theoretical model. A physically more sound criterion for clustering is the condensation scaling parameter Γ^* which combines the thermodynamics and kinetics of the condensation process. As discussed in the previous section, its

range $200 < \Gamma^* < 1,000$ is the barrier between free jets without and with formation of clusters. A comparison between the predictions based on the value of the nucleation rate J and on the value of Γ^* shall be made for the data of [17]. There J is given as function of expansions ratio for free jets starting from the saturated vapor at $p_0 = 1,200$ Pa. For the entire range of p_0/p , Ar had always the lowest J , followed by Ag, Pb and Al. The maxima of J varied between $5 \cdot 10^{24}$ and $5 \cdot 10^{26} \text{ m}^{-3} \text{ s}^{-1}$. This is then interpreted as the metals being more likely to produce clusters compared to the rare gas Ar. The respective numbers for the condensation scaling parameter Γ^* predict just the opposite behaviour: Assuming a nozzle diameter $d = 2$ mm yields the following values for Γ^* :

Ar: 1,027; Pb: 41.9; Al: 29.3; Ag: 26.3.

Thus all metals are unlikely to show free-jet clustering under these conditions, while Ar is predicted to be in the range of massive cluster production. The differences in Γ^* are primarily caused by the different densities n_0 , with Ar, due to the low vapor temperature, having about 30 times as many atoms per volume compared with Ag at the same pressure. To summarize this discussion the present state of condensation theory does not allow to make definitive predictions about clustering in free jets of gases or metal vapors. On the other hand, the available experimental information on clustering in free jets is well correlated by the condensation scaling parameter Γ^* .

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