

# CLUSTER GROWTH IN EXPANDING COPPER VAPOR

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Received: December 05, 2002

**Abstract.** Atomic clusters have been proposed as building blocks for tailor-made materials with specific combinations of properties. Growth of such clusters from vapor must be understood to enable one to prepare such materials. Here the process of the cluster growth in expanding copper vapor is analyzed by solving the balance equations for atoms, diatomic molecules, and clusters of different sizes as functions of temperature of buffer gas atoms and clusters. Dependence of the average cluster size at the end of the process on expansion time and the initial number density of atoms is studied. Numerical calculations are performed to obtain the realistic character of change of vapor parameters in a jet nozzle.

## 1. INTRODUCTION

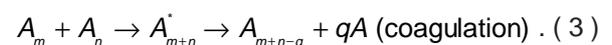
Intense cluster beams are generated in expanding vapors from an oven-formed atomic vapor [1], in gaseous discharge [2], or as a result of laser vaporization of a metallic surface [3]. When clusters are being nucleated under almost equilibrium conditions, there exists a critical radius for the clusters such that the cluster grows if its size exceeds the critical one and it evaporates when the size is below the critical radius [4]. Presence of nuclei of condensation (such as ions) in a weakly ionized gas accelerates this process dramatically. In the case of a jet expansion, such nucleation is not as essential because a strong super saturation of vapor makes the critical cluster size to be that of the order of an atom. Therefore, the concept of the critical radius is not as important for jet expansions.

The kinetics of the condensation process in free jet expansion has been analyzed in earlier papers [5-9]. Developing the scheme of kinetics of this process [6,7], in this paper we analyze this including some of their special behaviors. We perform numerical calculations for the case of copper vapor because beams of copper atoms have been used in microelectronics for deposition [10] and detailed

analyses of the parameters of copper clusters are available. These analyses include photoelectron spectroscopy of both cationic [11] and anionic [12-15] copper clusters. These also provide data from numerical calculations of the structure and binding energies of copper clusters and their ions [16-19]. In addition, parameters of cluster excitation due to transition of internal d-electrons are available from experiments and theories. This excitation energy is ~1 eV. Therefore, these states will be of importance for processes of cluster relaxation.

## 2. PROCESSES FOR CLUSTER GROWTH

The following processes with atoms, molecules, and clusters have been considered.

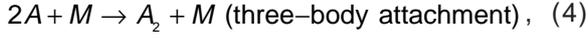


We assume that as a result of pair collision of a cluster with an atom, a molecule, or another cluster, a complex with a long life time is formed. During

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its life time, rearrangement in its internal degrees of freedom takes place leading to different resultant products. But during the first stages of cluster growth, when molecules are formed from atoms, three-body processes for the formation of molecules must be taken into consideration. In this case, the following processes are of importance for the evolution of diatomic molecules:



where  $M$  is an atom of a buffer gas. Note that because three-body processes are weaker than pair ones, processes (4) and (5) can delay the cluster growth remarkably [7].

On the basis of this scheme, the following balance equations are written down with the number density of atoms,  $N_1$ , of diatomic molecules,  $N_2$ , and of clusters consisting of  $n$  atoms,  $N_n$ :

$$\begin{aligned} \frac{dN_1}{dt} = & -\frac{N_1}{\tau_{ex}} + \sum_{m=3}^{\infty} N_m v_m \\ & -N_1 \sum_{m=2}^{\infty} N_m k_{1m} + \sum_{m,n} qk_{mn} N_m N_n \\ & -2KN_1^2 N_b + 2k_{dis} N_b N_2, \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{dN_2}{dt} = & -\frac{N_2}{\tau_{ex}} + 2KN_1^2 N_b \\ & -k_{dis} N_b N_2 + N_3 v_3 - N_1 N_2 k_{12} \\ & -N_2 \sum_{m=2}^{\infty} N_m k_{2m}, \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{dN_n}{dt} = & -\frac{N_n}{\tau_{ex}} + N_n N_1 k_{1n} \\ & -N_{n+1} v_{n+1} - N_{n-1} N_1 k_{1,n-1} - N_n v_n \\ & -2N_n \sum_{m=2}^{\infty} N_m k_{nm} + \sum_{m=2}^{\infty} N_m N_{n-m} k_{m,n-m}. \end{aligned} \quad (8)$$

Here  $N_b$ ,  $\tau_{ex}$ ,  $n_m$ ,  $k_{1m}$ ,  $k_{mn}$ ,  $K$ , and  $k_{dis}$  respectively represent the number density of atoms of a buffer gas, the expansion time, the probability of evaporation of a cluster of  $n$ -atoms per unit time [process (2)], the rate constant of electron attachment to a cluster of  $m$ -atoms [process (1)], the rate constant of joining of two clusters of sizes  $m$  and  $n$  [process (3)] which is accompanied by a release of  $q$  elec-

trons], the rate constant of the three-body process [process(4)], and the rate constant of dissociation of diatomic molecules resulting from collisions with an atom. As the last two terms of Eq. (8) describe processes without the participation of atoms, the last term of this equation corresponds to  $n$  starting from 4.

The balance Eqs. (6)-(8) also require to be modified suitably to include the change of the temperature of the gas. Because of a strong temperature dependence of the rate constants of cluster detachment, the cluster growth starts at temperatures when the rates of growth processes due to atom attachment to clusters become close to the order of the rates of processes of cluster destruction due to evaporation. The cluster growth stops when the cluster density becomes small due to gas expansion and due to the cluster growth process.

The following points about these balance equations are noteworthy. The cluster number densities are normalized such that in the absence of expansion, the total number density of atoms in clusters (but not the total number density of clusters) is conserved. It means that the equation

$$\sum_n n \frac{dN_n}{dt} = -\sum_n n \frac{N_n}{\tau_{ex}} \quad (9)$$

must follow from Eqs. (6)-(8). Therefore, a factor of 2 has to be multiplied to terms related to cluster loss. In the case of process (3), during the process of release of energy, atoms are also released. The number of released atoms  $q$ , is small compared with  $m$  or  $n$ . However, this process becomes substantially important at large values of  $m$  and  $n$ . Assuming  $N_n$  to be a smooth function of  $n$  for large values of  $n$ , in the last term of eq. (8) the value  $n-m+q$  is replaced by  $n-m$ . Eq. (9) means that the total con-

centration of free and bound atoms,  $c = \sum_{n=1}^{\infty} nN_n / N_b$ , is conserved during the process of cluster evolution.

The rates of processes (1) and (2) as well as the rates of processes (4) and (5) are related by the principle of detailed balancing. From this principle we have the following relation among these rates:

$$\frac{k_{dis}}{K} = \left( \frac{N_1}{N_2} \right)_{eq} = N_m \exp\left(-\frac{\epsilon_2}{T}\right), \quad (10)$$

where the suffix *eq* denotes the thermodynamic equilibrium between atoms and diatomic molecules (*Saha's relation*) and  $\epsilon_2$  is the dissociation energy

of the diatomic molecule. Using the parameters [20,21] for  $\text{Cu}_2$  molecules in Eq. (10), we have  $N_m = 2.3 \cdot 10^{23} \text{ cm}^{-3}$ ,  $\varepsilon_2 = 2.08 \text{ eV}$ . Thus, it is enough to obtain the rate constant  $K$  for the description of the processes of formation and dissociation of diatomic molecules. Based on previous analysis [22], one can accept its value to be  $10^{-33} \text{ cm}^6/\text{s}$  within an accuracy factor of 2. Therefore, we have used two values of this rate constant ( $1 \cdot 10^{-33} \text{ cm}^6/\text{s}$  and  $2 \cdot 10^{-33} \text{ cm}^6/\text{s}$ ) in the present calculations.

The relation between the rates of attachment and those of evaporation has the following form according to the principles of detailed balancing:

$$\frac{v_{n+1}}{k_{1n}} = \left( \frac{N_1 N_n}{N_{n+1}} \right)_{\text{eq}}. \quad (11)$$

We have used this relation for the thermodynamic equilibrium between clusters at large cluster sizes. In this case, Eq. (11) takes the form [22,23]:

$$\frac{v_{n+1}}{k_{1n}} = N_{\text{sat}}(T) \exp\left[ \frac{Q - \varepsilon_n}{T} \right], \quad (12)$$

where  $N_{\text{sat}}(T)$  is the atom number density corresponding to the pressure of saturated vapor at a given temperature and  $\varepsilon_n$  is the atom binding energy in a cluster consisting of  $n$  atoms. The number density of atoms at the pressure of saturated vapor can be approximated by the following Eq. [24]:

$$N_{\text{sat}}(T) = \frac{p_0}{T} \exp\left( -\frac{Q}{T} \right).$$

For liquid copper, the parameters of this equation are given by  $Q=3.26 \text{ eV}$  and  $p_0=7.1 \cdot 10^5 \text{ atm}$ . Note that if we use Eq. (12) instead of (10) (i.e. within the limits of its validity), we obtain  $N_m=1.4 \cdot 10^{24} \text{ cm}^{-3}$  instead of  $2.3 \cdot 10^{23} \text{ cm}^{-3}$ . This shows the accuracy of the equation for small clusters.

One can combine Eqs. (10) and (12) such that at  $n=2$  Eq. (12) can be written in the form:

$$\frac{v_{n+1}}{k_{1n}} = \frac{p_0}{T} \exp\left[ -\frac{\varepsilon_n}{T} + \frac{a}{n} \right]. \quad (13)$$

For copper,  $a=3.61$ . Due to the last term in the exponent of this equation it can be used for small clusters.

The main parameters of the above equations are related to the binding energies of cluster atoms. Introducing the cohesive energy of a large cluster of  $n$ -atoms the usual way [25],

$$E(n) = \varepsilon_n - \Delta\varepsilon n^{2/3}. \quad (14)$$

Parameters of this equation can be determined from bulk values.  $\varepsilon$  is the sublimation energy for one atom and  $\Delta\varepsilon=1.35 \text{ eV}$  is related to the bulk surface tension. Using the data for liquid copper [24], we have  $\varepsilon=3.13 \text{ eV}$  and  $\Delta\varepsilon=1.35 \text{ eV}$ . The physics of the evaporation process demands that the parameter  $Q$  must be approximately equal to  $\varepsilon+T_m$ ,  $T_m$  being the melting point of copper. From this equation we have  $Q=3.25 \text{ eV}$  that coincides with the above value within the limits of the accuracy of these equations and parameters.

The binding energy for the cluster atom is given by  $\varepsilon_n=E(n) - E(n-1)$ . Replacing  $n$  by its effective value  $n_{\text{eff}}=n-\delta$  we get

$$\varepsilon_n = \varepsilon - \Delta\varepsilon \left[ (n-\delta)^{2/3} - (n-\delta-1)^{2/3} \right], \quad (15)$$

$$\varepsilon_1 = 0.$$

This is similar to the expansion used in obtaining Eq. (14) with one more term included during the expansion. Choosing parameter  $\delta$  so that for  $n=2$ , Eq. (15) gives the measured dissociation energy of the diatomic molecule ( $\varepsilon_2=2.08 \text{ eV}$  [20,21] for copper), we obtain  $\delta=0.8$ . Eq. (15) is not valid for small values of  $n$ , and it is more correct to use realistic values.

Table 1 presents the binding energies of cluster atoms obtained using Eq. (14). From comparison of these data with those from different calculations, it is noticed that the accuracy of these results is not sufficient for us to use these for the analysis of the processes under consideration. Therefore, we have used the cluster binding energy based on Eq. (15) for later calculations.

For the rate constant of the attachment (process 1) and coagulation (process 3), we use the liquid drop model for clusters. According to this model, a collision of two clusters is like that of two liquid drops. The clusters combine to produce a complex in which the internal energy of the colliding clusters is redistributed among the various degrees of freedom of the complex, and this leads to further processes. This is an indirect use of the assumption of statistical mechanics that during the collision of two clusters, the first stage of the process leads to the formation of a complex with a sufficiently large life time. It is valid in this case because the collision energy of clusters (of the order of  $T$ , the thermal energy of particles) is small compared to the energy of a bond ( $\sim \varepsilon$ ).

This model may raise some questions. The first one is related to the magic numbers observed in

**Table 1.**

Atom binding energy (difference between the total binding energies of  $\text{Cu}_n$  and  $\text{Cu}_{n-1}$ ) in copper clusters (in eV).

Cluster	Ref. 16	Ref. 17	Ref. 19	Eq. (15)
$\text{Cu}_2$	1.05	0.46	3.02	2.08
$\text{Cu}_3$	0.52	2.08	1.87	2.37
$\text{Cu}_4$	1.61	2.58	3.47	2.48
$\text{Cu}_5$	1.33	3.03	3.29*	2.55
$\text{Cu}_6$	1.69	2.21	3.29*	2.59
$\text{Cu}_7$	1.80	3.31	3.79*	2.63
$\text{Cu}_8$	1.67	4.43	3.79*	2.65
$\text{Cu}_9$	2.24	2.92*	3.29*	2.67
$\text{Cu}_{10}$	1.99	2.92*	3.29*	2.69

\*The binding energy is averaged over the neighboring numbers of atoms.

the case of small clusters where cluster parameters are not monotonic functions of size. Next, the liquid drop model is based on a spherical average shape for the cluster which may not be valid always. The first objection can be met by using the real binding energies of clusters,  $\epsilon_n$ . Unfortunately, experimental data are available only for small ranges of cluster sizes. We, therefore, have decided to use the values of  $\epsilon_n$  averaged over sizes. By this averaging, the deviation from spherical form of the clusters becomes unimportant for liquid clusters.

The last fact has been demonstrated clearly by a measurement of the mobility of positive aluminum cluster ions in helium [26,27]. In this case, for most of the cluster sizes, the hard sphere model has explained the results of measurement very well. But for some sizes ( $n = 27, 45, 46$ ) of clusters, the measured mobility exceeds the result of the hard sphere model. It has been proposed that nonspherical cluster structures should be considered for these sizes at small temperatures. However, increase of temperature causes a transition to spherical cluster structures and the activation energy for this transition is 0.5-0.7 eV. Thus the effect of nonspherical structures is not important if the result is averaged over cluster sizes or at high temperatures.

It is clear that each contact of two clusters leads to a formation of a complex because the collision energy is small compared to the energy of each bond between clusters, and several bonds can be formed as a result of a collision. But if an atom collides with the cluster surface it can also be reflected. Hence it is necessary to introduce in the theory the probability of an atom being attached to a cluster

after collision. Due to lack of such information, we assume this probability to be unity. In order to estimate the error of this assumption, let us consider this effect for attachment of tungsten atoms to the surface of liquid bulk tungsten. Then from data [24] for the rate of tungsten vaporization and the pressure of the saturated vapor, it follows that the attachment probability is equal to approximately 0.6 in the temperature range of 2500 - 3500K. From this value one notes that our assumption for copper is equivalent to an error of about 0.04 eV in the binding energy. Evidently, this error will not influence our results under study.

Within the framework of the model under consideration, we assume that the densities of atoms in clusters and bulk liquid are the same. Then the rate constant of the process (3) [or (1)] is given by [22,28]:

$$k_{nm} = k_0 \left( \frac{T}{T_0} \right)^{1/2} f_{nm}, \quad (16)$$

$$f_{nm} = (n^{1/3} + m^{1/3})^2 (m+n)^{1/2} m^{-1/2} n^{-1/2}.$$

Here

$$k_0 = 1.93 T_0^{1/2} m^{1/6} \rho^{1/3}, \quad (17)$$

where  $m$  is the atomic mass and  $\rho$  is the density of the cluster material. We use the melting point as  $T_0$ . For copper  $k_0 = 3.6 \cdot 10^{-11}$  cm<sup>3</sup>/s. To obtain Eq. (17), we have assumed the cross section of coagulation as  $\pi r^2$ , where  $r$  is the sum of the radii of the colliding clusters. The radius of a cluster of  $n$  atoms,  $r_n$ ,

is given by the following expression in a liquid drop model:

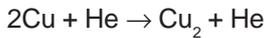
$$n = \frac{4\pi r_n^3}{3m} \rho. \quad (18)$$

Joining of two clusters at a certain temperature leads to the formation of a complex cluster with a higher temperature because it has lower surface energy. This complex can, therefore, decay through evaporation of single atoms because the probability of evaporation of diatomic molecules and clusters is very small. Let us assume that the evaporation of atoms from a cluster proceeds until the temperature reaches the temperature of initial clusters. Then the number of released atoms in process (3) is an integer given by:

$$q = \frac{\Delta\varepsilon [m^{2/3} + n^{2/3} - (m+n)^{2/3}]}{\varepsilon_{m+n}}. \quad (19)$$

Note that the value  $q$  is relatively small. For example, for  $m=n$  in the case of copper,  $q=1$  for  $m=12$ ,  $q=2$  for  $m=34$ , and  $q=3$  for  $m=63$ . For this reason we neglect this process in the balance equation for clusters (Eq. (8)). But it is an important channel for generation of free atoms and is taken into account in the balance equation for atoms (Eq. (6)).

The rate constant of the three-body process requires a special analysis. According to the analysis [22] of measured rate constants of three-body processes at high temperatures, the rate constant depends on the temperature only weakly and is equal to  $10^{-33}$  cm<sup>6</sup>/s with an accuracy factor of 2. According to the Troe analysis [29] for a more wide range of temperatures, the average rate constant can be approximated by the relation  $K=10^{-33}$  cm<sup>6</sup>/s ( $T/1000$ K), and its accuracy is within a factor of 3. A rough estimation of the rate constant of the process



gives  $K \sim 4 \cdot 10^{-33}$  cm<sup>6</sup>/s at a temperature of 300K. Using the above information, we use two values for the three-body rate constants ( $1 \cdot 10^{-33}$  cm<sup>6</sup>/s and  $2 \cdot 10^{-33}$  cm<sup>6</sup>/s) in our calculations.

Now let us consider the nature of the process of cluster growth during the expansion of a vapor. Initially, the atomic vapor expands in the form of a beam and the temperature is sufficiently high so that the equilibrium state of this vapor corresponds to the atoms only. As the vapor is cooled due to expansion, it condenses to cause the formation of clusters starting with diatomic molecules. The pro-

cess of the cluster growth stops when the expansion and cluster formations deplete the atomic beam so that the concentration of atoms falls below a critical value. Then the cluster density also decreases due to further expansion, but the distribution of cluster sizes does not change. The vapor temperature decreases through transition of its thermal energy into mechanical. The value of this energy per atom is of the order of the atomic thermal energy ( $kT$ ) if the initial and final gas pressures differ strongly. But as a result of cluster formation, the energy released is of the order of cluster binding energy ( $\varepsilon$ ) for each atom. As  $\varepsilon \gg kT$ , the nucleation of the vapor is impossible in the absence of a buffer gas. It is the buffer gas which expands with the vapor and takes away the excess energy making the cluster formation possible.

### 3. HEAT REGIMES OF NUCLEATION

Let us consider the heat regime of the nucleation process during the expansion of a vapor in detail. We obtain the relation between the number density of a buffer gas  $N_b$  and the gas temperature as done before [30] for the formation of diatomic molecules. Let us use gas of volume  $V$  which contains  $n_b$  atoms of a buffer gas and  $n_v$  atoms of vapor so that the concentration of vapor atoms at the beginning  $c=n_v/n_b$  is small ( $c \ll 1$ ). The change of the total energy of this volume during expansion is given by

$$dE = dQ + pdV, \quad (20)$$

where  $Q$  is the thermal energy of particles in this volume,  $p$  is the gas pressure. Neglecting the thermal energy of vapor atoms we have for monatomic buffer gas:

$$dQ = \frac{3}{2} n_b dT - \sum_{k=1}^{\infty} E_k dn_k,$$

where  $n_k$  is the number of clusters containing  $k$  atoms and  $E_k$  is the total binding energy of the cluster given by Eqs. (14) and (15). Introducing the number density of buffer gas atoms  $N_b=n_b/V$  and using the condition  $dn_b=0$ , for the second term of Eq. (20) we have  $pdV=-n_b T dN_b/N_b$  (from the equation of state of the gas:  $p=N_b T$ ). Because of the adiabatic character of the expansion process  $dE=0$ . From the above condition and Eq. (20) we have:

$$\frac{3}{2} n_b dT - \frac{n_b T dN_b}{N_b} - \sum_{k=1}^{\infty} E_k dn_k = 0. \quad (21)$$

This equation gives the relation between the temperature and the number density of a buffer gas

during expansion. If one can neglect the influence of the nucleation process on the thermal expansion, one gets the well-known law of the adiabatic expansion of an atomic gas [31]:

$$N_b \sim T^{3/2}. \quad (22)$$

Let us consider the case of an expanding gas in a beam of a radius  $R$ . The radius is related to the temperature of the gas. As the total number of atoms is conserved, the atom flux  $J = \pi R^2 N_b u$ , where  $u$  is the drift velocity of atoms in the beam. Assuming  $u$  to be independent of temperature, we obtain:

$$\frac{N_b}{N_0} = \frac{R_0}{R^2}. \quad (23)$$

Substitution of this in Eq. (21) leads to:

$$\frac{3}{2} n_b dT + 2n_b \frac{TdR}{R} - \sum_{k=1}^{\infty} E_k dn_k = 0. \quad (24)$$

Let the initial values of  $R$  and  $T$  be  $R_0$  and  $T_0$  respectively. Assuming that in the beginning there were only free atoms and at the present moment all the atoms are in clusters, the solution of Eq. (24) is given by:

$$T = T_0 \left( \frac{R_0}{R} \right)^{4/3} \exp\left( \frac{2\varepsilon c}{3T^*} \right), \quad (25)$$

where  $T^*$  is the temperature of condensation and  $\varepsilon$  is the mean binding energy of cluster atoms per atom. In solving Eq. (24), we have assumed that the entire condensation process proceeds at this temperature and the binding energy of molecules and clusters per atom,  $\varepsilon$ , does not depend on the cluster size.

From Eq. (25) it follows that the nucleation process does not influence the thermal regime of expansion of the buffer gas if the following criterion is satisfied:

$$C \ll \frac{T}{\varepsilon}. \quad (26)$$

Under laboratory conditions, it means that the concentration of the vapor must not exceed more than only a few per cent of the concentration of the buffer gas. Otherwise, the expansion of the gas will get completed at a relatively high temperature and only a partial condensation of the vapor will occur.

In summary, the condensation process does not influence the evolution of the number densities of atoms, but changes the ultimate temperature of the gas because of the heat released in this process. The balance equation for the number density of atoms of a buffer gas (as well as for that of total number of vapor atoms) has the form:

$$\begin{aligned} \frac{dN_b}{dt} &= -\frac{N_b}{\tau_{ex}}, \\ \frac{dT}{dt} &= -\frac{2T}{3\tau_{ex}} + \sum_{n=2}^{\infty} \frac{E_n}{N_b} \frac{dN_n}{dt}, \end{aligned} \quad (27)$$

where  $E_n$  is given by Eq. (14). If the criterion (26) is satisfied, the nucleation process does not influence the temperature of a buffer gas. Let us consider its influence on the cluster temperature. Consider a large cluster and the regime of the expansion process when the evaporation process is weak compared to that of atom attachment. Then each attachment act leads to an increase of the cluster internal energy by the value  $\varepsilon_n$ , the binding energy of an attached atom. Collisions with atoms of a buffer gas equalize this process. Let us assume that the mean atomic energy after a collision is  $3T_n/2$ , where  $T_n$  is the cluster temperature. Then from the equality of the above fluxes we have:

$$\frac{3}{2}(T_n - T)N_b m^{1/2} = \varepsilon_n N_1 m_b^{1/2}, \quad (28)$$

where  $m$  and  $m_b$  are the masses of atoms of vapor and of a buffer gas respectively. This equation corresponds to the condition  $N_b \gg N_1$ . If the criterion (26) is satisfied, the difference between the cluster and gas temperatures is small compared to the gas temperature. But because of a strong temperature dependence for the evaporation constant, this effect must be taken into account.

#### 4. EXPANSION OF VAPORS FROM A NOZZLE

The expansion time  $\tau_{ex}$  in balance Eqs. (6), (7), (8), and (27) depends on time and the nature of expansion of a gas. If the condensation process takes place in a narrow range of temperature,  $\tau_{ex}$  can be taken as a constant. In order to understand the validity of this approximation, we consider below the behavior of this parameter while a vapor expands from a nozzle.

Note that the character of vapor expansion in a vacuum depends on the nozzle profile [32,33]. We will be guided below by the hyperbolic form of a nozzle which is used more often than the other ones. Besides, all the expressions below relate to monatomic gases only. The flux of a plume expanding from a nozzle with a velocity  $u$  is given by the expression:

$$u = \frac{v_0}{1 + 3/M^2}, \quad (29)$$

where  $v_0 = \sqrt{5T/m}$ ,  $m$  is the atomic mass and  $M$  is the Mach number. The Mach number increases with distance from a nozzle and is large ( $M \gg 1$ ) at large distances from the nozzle. According to Wiel [5], the dependence of the Mach number on a distance  $x$  from a nozzle is given by:

$$M = 1 + 2.82\delta \tan \alpha, \quad (30)$$

where  $\delta = x/d$ ,  $d$  is the nozzle diameter and  $2\alpha$  is the total opening angle of the nozzle. This equation is valid up to  $\delta = 15$ . At larger distances one can use Hagena's [34] asymptotic expression:

$$M = 2.72 \delta^{2/3}. \quad (31)$$

The dependence of parameters of an expanding vapor on a distance from the nozzle can be expressed through the Mach number. In particular, in the absence of condensation, the vapor temperature is [35]:

$$T = \frac{T_0}{1 + M^2/3}. \quad (32)$$

Using it in Eq. (27) for the gas temperature, one can obtain the expression for  $\tau_{ex}$  in a wide range of distances from a nozzle. Usually Eq. (31) is violated for very large values of  $\delta$ . When  $\delta$  gets close to infinity, the Mach number and the gas temperature approach finite values [36]. This may be an important point for the condensation process.

A convenient scaling law for vapor parameters during a free jet expansion was suggested by Hagena [37]. The basis of this procedure is such that on the basis of three gas parameters one can construct reduced parameters of a gas and by these reduced parameters one can describe the time evolution of the gas. Hagena used the bulk binding energy per atom  $\varepsilon$ , the bulk density  $\rho$ , and the atomic mass  $m$  as the gas parameters. Taking it into account and based on experimental data, Hagena [37] chose combinations of parameters through which one can express characteristics of condensation for different gases and vapors. One such parameter is

$$\dot{\psi} = \frac{\psi}{\psi_{ch}} \quad \text{with} \quad \psi = N_0 d T_0^{-1.25}. \quad (33)$$

Here  $N_0$  is the initial number density of atoms,  $T_0$  is the initial temperature, and  $d$  is the nozzle diameter. The parameter  $\psi_{ch}$  is constructed from the above parameters of the gas and  $\psi_{ch} = 1.7 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{K}^{-1.25}$  for argon, while  $\psi_{ch} = 3.3 \cdot 10^9 \text{ cm}^{-2} \cdot \text{K}^{-1.25}$  for copper. The parameter  $\psi$  determines the final gas temperature from a nozzle [37] as

$$T_\infty = 0.6 T_{ch} (\psi^*)^{-0.8}, \quad (34)$$

where  $T_{ch}$  characterizes the binding energy of large clusters. This value is equal to 930K for argon and  $4.06 \cdot 10^4$  for copper. These relations are conveniently used for the analysis of the condensation process.

To demonstrate the usefulness of the above equations, let us analyze the condensation of copper under conditions of the experiment [38]. In this experiment, condensation of copper was studied up to the formation of dimers. The initial vapor temperature, vapor pressure, and the nozzle diameter were given by  $T_0 = 2500\text{K}$ ,  $p_0 = 100 \text{ Torr}$ , and  $d = 0.625 \text{ mm}$  respectively. According to Eq. (34), these parameters correspond to the final temperature of copper vapor  $T_\infty = 330\text{K}$ . One can then consider the temperature when the condensation starts coincides with the vibrational ( $T_{vib}$ ) or rotational ( $T_{rot}$ ) temperatures of dimers when their concentration is small. According to the above experiment for copper these parameters are [38]  $T_{vib} = 950 \pm 100\text{K}$  and  $T_{rot} = 800 \pm 50\text{K}$ . From Eq. (25) it follows that due to the condensation process the final temperature increases up to  $T_{min}$  which is given by the expression:

$$T_{min} = T_\infty \exp\left(\frac{2\varepsilon C}{3T^*}\right). \quad (35)$$

From this it follows that for the maximum concentration of dimers in the end of the process  $T^* = T_{min}$ ,

$$C < \frac{3T^*}{2\varepsilon} \ln \frac{T^*}{T_\infty}. \quad (36)$$

In this case  $\varepsilon$  corresponds to the dissociation of the diatomic molecule. For the case of maximum concentration of diatomic molecules, the above data and equations give  $c = 5-7 \%$ .

## 5. NATURE OF CLUSTER GROWTH

Let us consider the kinetics of the nucleation process. This process is guided by the typical times given by Eqs. (6)-(8), the expansion time  $\tau_{ex}$ , a typical time of attachment  $\tau_{at} \sim (k_0 N_1)^{-1}$ , the evaporation time  $\tau_n = 1/v_n$ , and a typical time of the three-body process  $\tau_3 \sim (KN_1 N_b)^{-1}$ . In the case of jet expansion, the expansion time  $\tau_{ex} \sim r/v_T$ , where  $r$  is the nozzle radius and  $v_T$  is the thermal velocity of atoms. Usually this time is of the order of  $10^{-7}-10^{-6} \text{ s}$ . The evaporation time depends strongly on the cluster temperature. Table 2 gives some values of the evaporation times for copper clusters which are calculated on the basis of the equations for large clusters [22,28]. It can be noticed that this value has a strong

**Table 2.**

The life time of copper clusters (in seconds) with respect to evaporation of an atom.

$T$ (K)	1000	1200	1400	1600
$n = 25$	$1.0 \cdot 10^{-2}$	$4.4 \cdot 10^{-5}$	$8.9 \cdot 10^{-7}$	$4.8 \cdot 10^{-8}$
$n = 50$	$1.4 \cdot 10^{-2}$	$5.1 \cdot 10^{-5}$	$9.5 \cdot 10^{-7}$	$4.8 \cdot 10^{-8}$
$n = 100$	$1.5 \cdot 10^{-2}$	$5.3 \cdot 10^{-5}$	$9.1 \cdot 10^{-7}$	$4.4 \cdot 10^{-8}$

dependence on the temperature and a weak dependence on the cluster size. The process of cluster growth starts at temperatures when  $\tau_{at} < \tau_n$ .

The nature of evolution of the system depends on the relation among the above times. Clusters are formed only when  $\tau_{ex} \ll \tau_{at}$ . Considering limited cases of evolution of the system, two reduced parameters may be defined:

$$\alpha = \frac{\tau_{ex}}{\tau_3} = N_1 N_b K \tau_{ex},$$

$$\beta = \frac{\tau_{ex}}{\tau_{at}} = N_1 k_{1n} K \tau_{ex}. \quad (37)$$

Here  $n$  is a typical cluster size. In accordance with the character of the process, the number densities are taken at a temperature where times of attachment and evaporation are of the same order of magnitude.

Usually  $\alpha \ll \beta$ . When  $\beta \ll 1$ , the process of cluster formation is weak. Then the number density of molecules and clusters in the end of the process is small. In the case  $\beta > \alpha \gg 1$ , all the atoms are transformed at first to diatomic molecules as a result of the three-body process (4). After that the diatomic molecules and small clusters are transformed into large clusters as a result of the coagulation process (3). If only the coagulation process is taken into account, the set of Eq. (8) can be changed into one integral equation, and its solution yields [22,23] the mean cluster size  $\bar{n}$ :

$$\bar{n} = 10(N_0 k_0 \tau_{ex})^{1.2}, \quad (38)$$

where  $N_0$  is the number density of vapor atoms when the coagulation process starts. The rate constant  $k_0$  is given by Eq. (17).

In the case  $\alpha \ll 1$ , only a small fraction of atoms is transformed into diatomic molecules as a result of the three-body process (4). After this, diatomic molecules and small clusters can both be

grown as a result of attachment of atoms (process (2)) and coagulation (process (3)). The mean cluster size is estimated from  $\bar{n} \sim \beta$  and has the same order of magnitude as that in Eq. (38). When  $\alpha\beta \gg 1$ , all the atoms in the end of the process are located in clusters. Besides, in this case, the coagulation process is of importance in the last stage of the cluster evolution. In the opposite limited case of  $\alpha\beta \ll 1$ , in the end of the process there are  $\sim \alpha\beta N_1$  clusters and  $\sim N_1$  atoms. Clusters are formed from diatomic molecules as a result of atom attachment, and the coagulation process does not proceed in this case. Thus the main part of atoms remain to be free and  $\sim \alpha\beta$  part of atoms are in the form of large clusters.

In order to make these general considerations more exact, a numerical solution of the set of eqs. (6)-(8) was obtained up to  $n=100$ . It allows one to obtain numerical parameters for the criterion  $\alpha$  of Eq. (37) at a temperature  $T_2$  such that  $k_{dis}(T_2) = KN_2(T_2)$ , i.e. according to Eq. (10), this temperature satisfies the relation  $N_1(T_2) = N_m \exp(-\delta_2/T_2)$ . For the formation of copper clusters, this temperature ranges from 1500K to 1700K. The temperature  $T_{cl}$  for the criterion  $\beta$  in Eq. (37) is chosen such that at this temperature the rates of atom attachment and atom evaporation are equal, i.e. according to Eq. (13),  $N_1(T_{cl}) = (p_0/T_{cl}) \exp(-\epsilon/T_{cl})$ . For the case of copper under consideration,  $T_{cl}$  lies between 2200-2400K. Thus  $\alpha = N_b(T_2) N_1(T_2) K \tau_{ex}$  and  $\beta = N_1(T_{cl}) k_0 \tau_{ex} n^{1/6}$ , where  $n$  is the average cluster size.

Let us examine the results of calculations through the above parameters. The fraction of atoms which transform into clusters at the end of the process is given by

$$\frac{N_{cl}}{N_1} = \frac{C_1 \alpha \beta}{1 + C_1 \alpha \beta}, \quad (39)$$

where the numerical parameter is equal to  $c=11 \pm 1$ . The average size of clusters is determined by the equation  $\bar{n} = C_2 \beta$ , from which

$$\bar{n} = \frac{\sum_{n=2}^{\infty} n^2 C_n}{\sum_{n=2}^{\infty} n C_n}, \quad (40)$$

where  $C_2=4$ , if the main process of the cluster growth is due to the attachment of atoms to clusters, and  $C_2=5$ , if the cluster growth is mainly due to the coagulation of clusters. The analytical method [22] gives  $C_2=4.3$  in the last case.

Note a strong dependence of the degree of clusterization on the vapor pressure. To show this, we give some results. Take the vapor concentration in a buffer gas to be 1%, and consider a free jet expansion of copper vapor with a buffer gas through a nozzle of diameter 1 mm (which corresponds to an expansion time  $\tau_{ex}=8 \cdot 10^{-7}$  s, and the typical temperatures in this case are  $T_2=1700\text{K}$ ,  $T_c=2200\text{K}$ ). Taking the rate constant of the three-body process  $K=10^{-33}$  cm<sup>6</sup>/s, we find that one half of the atoms is transformed into clusters if the copper vapor pressure at the beginning of clusterization is equal to 30 Torr. If this pressure is 8 Torr, only 1% of the atoms are transformed into clusters at the end of the process. From this one can also conclude that laser vaporization is a more suitable process for generation of copper cluster beams than a free jet expansion.

In conclusion, this analysis shows that the first stage of the process with the three-body formation of molecules is of importance. Also the heat regime of the process can determine the cluster evolution at high vapor concentration or in the absence of a buffer gas. Therefore, weak formation of molecules may delay the cluster growth process. Hence the presence of molecular particles in the vapor flux at the beginning may accelerate the cluster growth process remarkably. One more conclusion from this fact is related to the need of analyzing the first stage of the process carefully. For example, in the experiment on expansion of copper vapor [30] resulting from laser ablation of a copper target, at typical number densities of atoms  $N_1 \sim 10^{15}$  cm<sup>-3</sup> and typical diatomic number densities  $N_2 \sim 10^{11} - 10^{12}$  cm<sup>-3</sup>, Cu<sub>3</sub> clusters were not observed while the limit of the number density for their detection is of the order of  $N_3 \sim 5 \cdot 10^9$  cm<sup>-3</sup>. One possible explanation of this fact is that under conditions of the experiment Cu<sub>3</sub> clusters are not formed in pair collisions. But according to the presented theory, these clusters are formed just as a result of pair collisions. Thus, this scheme may need to be revised after obtaining more accurate data on the binding energies and the rate constants for some cluster processes. At the present level of accuracy of the binding energies for small copper clusters, we cannot analyze this process for small clusters even within the framework of the liquid drop cluster model.

In spite of the problems of description of small clusters, this scheme allows one to describe this process for large clusters. It is universal and can be used for various metallic vapors by simply taking into account the corresponding data for the binding energies. Besides, it gives simple estimations for

the mean cluster size under certain conditions of the process.

## ACKNOWLEDGMENTS

The work was partially supported by a grant from the U. S. Department of Energy (DE-FG02-96ER45579) and by a grant-in-aid from Virginia Commonwealth University.

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