Processes in expanding and condensing gases

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Abstract. The evolution of a hot gas or weakly ionised plasma — formed as a result of vaporisation of the surfaces of a solid under the action of high energy fluxes or flow out of a nozzle — is considered. The expansion of a vapour or a plasma into the surrounding space leads to its cooling and is accompanied by a chain of processes involving both charged (electrons, ions, atoms, charged clusters) and neutral particles. The evolutionary regimes leading to the condensation of atoms, accompanied by the formation of large charged and neutral clusters, are discussed. The experimental aspects of the generation of intense cluster beams in such regimes and the applications of such beams are considered.

1. Introduction

This review provides an analysis of the processes that accompany the flow of a hot gas in vacuum or of a buffer gas under conditions such that clusters form in an expanding gas. The process of formatting clusters in an

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Received 21 June 1993; revision received 21 February 1994 Uspekhi Fizicheskikh Nauk **164** (7) 665-703 (1994) Translated by A Tybulewicz expanding atomic beam is most effective in the presence of ions which act as condensation nuclei. The simplest method for the generation of a cluster beam involves irradiating a surface with laser radiation of moderate intensity so that the surface temperature reaches several thousands of degrees celsius. This results in intense vaporisation of the surface, so that the vapour pressure near the surface amounts to tens and hundreds of bars. The evaporated material forms a beam of atoms which, because of the high surface temperature, contains a small admixture of ions. These ions then act as condensation nuclei. Another way of generating a cluster beam involves the use of a source of a gas or vapour inside a closed vessel out of which a gas (vapour) flows through a nozzle. Clusters form in this beam in the course of expansion of the gas jet.

Cluster beams were first generated in Germany [1-3] during the escape of a vapour, formed in a source, through a small nozzle into vacuum. The methods of beam analysis by determination of the mass spectra of the ions formed as a result of collisions of clusters with electrons were developed in the course of these investigations. The subsequent evolution of this technique [5-9] has included both modification of the vapour source and beam formation methods, and also methods for the detection of a cluster beam. Additional ionisation of an expanding vapour beam by an electron beam has led to the development of the 'cluster ion (ionised cluster) beam' method [10-11] and its various applications. A beam of charged clusters is convenient because ions can be accelerated by an external

electric field so as to reach the required energies of clusters in the beam. This makes it possible to employ a cluster beam colliding with the surface of a solid for a variety of purposes. Figs 1 and 2 demonstrate the nature of the interaction of an accelerated cluster with the surface, as a function of its energy [12]. At low energies (Fig. 1) the clusters are deposited on the surface and form a film, whereas at high energies (Fig. 2) they create clusters on the surface and cause its erosion. Therefore, cluster beams are used not only for the evaporation of films, but also for the cleaning of surfaces [10]. Cluster beams can be used to grow films at high rates up to 74 nm s⁻¹, as reported for silver clusters [13, 14], and the maximum rate of erosion by a focused beam of copper ion clusters is 70 nm^{-1} [15, 16].

The advantages of a cluster beam in the deposition of films, compared with an atomic beam, is the relatively small beam divergence because of the large cluster mass, and also



Figure 1. Model of a collision of a cluster with a surface, where it becomes attached and flows along it [12, 195]: (a) cluster disintegrates into single atoms which diffuse along the surface; (b) cluster behaves like a liquid drop, which becomes attached to the surface and spreads over it.



Figure 2. Collision of a fast cluster with the surface creates a shock wave which forms a crater on the surface (1) and a molten zone (2) at the crater boundary [12, 195].

the ability to control the beam in the case of charged clusters. Moreover, the energy released when a film is formed from clusters is several times less than in the case of formation of a film from single atoms. Therefore, the process of film growth from a cluster beam is more efficient and 'softer' than in the case of an atomic beam. This is the reason for the extensive use of cluster beams in microelectronics [5, 10, 11, 17-28].

There are also other applications of cluster beams such as those in thermonuclear fusion [7, 29-31], assembly of new materials from clusters [32, 33], formation of magnetic materials from clusters [34, 35], etc.

The purpose of this review is to consider the other aspect of the problem, which is the nature of the processes that accompany the expansion of a vapour in space. Various processes take place during the expansion of a vapour and formation of clusters, and combinations of these processes create specific nonequilibrium conditions. This will be demonstrated by considering the example of expansion and cooling of a weakly ionised vapour generated by laser irradiation of a surface. The processes will be divided into several groups in accordance with the stages of evolution of a weakly ionised vapour. The first group of processes, which corresponds to the first stage of the evolution of a weakly ionised plasma, includes those involving electron participation such as the ionisation of atoms by electron impact, the three-body recombination of electrons and atomic ions, the dissociative recombination of electrons and molecular ions, and the attachment of electrons to atoms producing negative ions. On completion of these processes a plasma containing electrons and atomic ions is converted into a plasma which consists of negative and positive ions.

The evolution of charged particles in such a plasma is important because ions serve as condensation nuclei in a cooling plasma. The second group of the processes includes charge exchange between positive and negative ions, which involves the loss of charged particles in a plasma and results in mutual neutralisation of ions. The processes of ion charge exchange occur simultaneously with the processes belonging to the third group, which represents the growth and evaporation of clusters. In this case the condensation represents the growth of charged clusters. In accordance with the classical theory of condensation [36-40], the probability of evaporation of a small neutral cluster is much higher than the probability of its growth. Therefore, large neutral clusters form in a weakly ionised gas not from small neutral clusters by growth, but from large charged clusters by coagulation. Neutral clusters form in a nonionised gas when it is strongly supersaturated, because this process requires a relatively high vapour pressure in the source.

An essential feature of the system under discussion is its nonequilibrium in respect of the various degrees of freedom at different stages of the evolution. By way of illustration, the ionisation nonequilibrium will be considered first [41 - 43]. During the first stage of plasma expansion, when the plasma temperature is sufficiently high, an ionisation equilibrium is established so that the densities of electrons and ions are described by the Saha distribution. The time needed to establish this equilibrium is inversely proportional to the electron density, i.e. it rises strongly when the plasma temperature decreases. At some temperature this time becomes comparable with the plasma expansion time, so that at lower tem-peratures the ionisation equilibrium in the plasma is lost, i.e. the densities of electrons and ions are governed not by the plasma temperature but by the nature of the plasma evolution. It is important to stress that the subsequent processes involving electrons occur in a nonequilibrium plasma and that the charged particles still act as the condensation nuclei.

An analysis of the formation of clusters in the course of the plasma evolution and allowance for the specific sequence of the processes that occur in the plasma makes it possible to provide a more or less unified physical picture of the evolution in spite of the fact that it is controlled by many processes. This is interesting from the point of view of understanding the nature of the evolution of the system and also in respect of the applications, which involve the optimal organisation of the process. This can be demonstrated by considering one of the aspects of the problem of the evolution of a laser plasma. The irreversible decay of the plasma electrons may occur in two channels: their conversion into negative ions or dissociative recombination with molecular ions. If the first channel is weak, then at the subsequent stage of the evolution there are a few ions that can act as the condensation nuclei in the plasma. Therefore, efficient conversion of the plasma into clusters requires that the formation of negative ions should occur in an effective manner. One example is the plasma-chemical conversion of metal compounds, which in the first stage are heated to high temperatures in a plasmatron, where these compounds dissociate into atoms. Then, the resultant plasma is allowed to escape. The condensation of metal atoms and ions transfers the metal to clusters and in this way the separation of elements is achieved. In view of the above comments it follows that this process is effective provided the atoms in the original compounds can form very stable negative ions. For example, if metal clusters are to be formed by this method, it is convenient to use metal halides.

The processes occurring in an expanding plasma jet lead to the formation of charged and neutral clusters. If the clusters remain for a long time in bounded space, the process can continue further resulting in the formation of structures consisting of solid particles in the form of fractal aggregates

[44-52] and fractal fibres [53, 54]. The process of forming fractal aggregates has been investigated quite thoroughly (there are reviews and monographs on this subject: see, for example, Refs [52-72]). In particular, the formation of fractal aggregates in the afterglow of a gas discharge increases strongly the yield of the radiation from a decaying plasma and the main contribution to the radiation power may come, in accordance with the dimensions of fractal aggregates, from the optical part of the spectrum (see, for example, the review in [73]). However, in the discussion below we shall consider only those stages of the process which are associated with cluster formation. This applies to systems in which an expanding gas or a plasma propagates in the form of a beam and in which condensation takes place, i.e. clusters are formed. This review provides an analysis of the processes which then occur.

2. Charged particles in an expanding plasma

2.1 Generation of a weakly ionised vapour near a heated surface

The initial stage of the processes under discussion is represented by a relatively dense gas (vapour) or an equilibrium plasma, which then expands in vacuum or in a space occupied by a buffer gas. In view of the applications, it is worth considering two methods for the creation of an expanding plasma. In the first method, the initial stage is the formation of a hot vapour (Figs 3 and 4) which expands through a nozzle in vacuum or in a buffer gas. A skimmer is used to form a gasdynamic beam of atoms from the vapour flux and ions may be created in this beam by an external electron source (Fig. 4). In the second method an ionised gas is formed by the interaction of high energy fluxes with a surface. The heating of the surface leads to the evaporation of its material in the form of a weakly ionised vapour. The energy can be delivered to the surface in the form of a laser beam, an electric current, an electron beam, etc.



Figure 3. Source of an expanding beam of neutral clusters [9]: (1) vapour flow; (2) deceleration chamber; (3) nozzle; (4) beam boundary.



Figure 4. Source of cluster ions [209]: (1) chamber; (2) heater; (3) nozzle; (4) skimmer; (5) electron beam; (6) accelerator of cluster ions. Caesium vapour forms by the evaporation of a liquid metal which is in the chamber.

Let us consider the second method of generating an expanding plasma in greater detail. The laser method is more convenient for the delivery of energy to a surface. Although the electric field method can also be used, it is more complex. In the electric field method the formation of an evaporated flux of a weakly ionised vapour takes place in the cathode spot of an arc discharge. The laser radiation creating a flux of the evaporated material does not interact with this material. This means that the power delivered is relatively low, so that laser radiation is not absorbed by the evaporating plasma. At higher laser radiation intensities, optical breakdown is possible because of the absorption of laser radiation by an evaporating weakly ionised plasma [74-76]. To avoid dealing with breakdown, we shall consider laser radiation intensities (power densities) not exceeding $10^7 \,\mathrm{W}\,\mathrm{cm}^{-2}$ on the surface [74-76].

One other aspect of the problem should be mentioned. Interaction of laser radiation with the surface heated by it is nonlinear. This may give rise to a number of interesting effects in the spatial temperature distribution on the surface of the investigated object and to fluctuations of the temperature with time (see, for example, Refs [77–79]). These effects will not be discussed and the temperature distribution on the surface of an object will be regarded as stable.

Let us consider the processes occurring near the surface. Let us assume that the range of the evaporating atoms is much less than the dimensions of the surface. This allows us to consider the evolution of the evaporating material as a one-dimensional problem. The energy flux reaching the surface heats it to a temperature† T_{surf} . This temperature corresponds to a flux of evaporating atoms $j(T_{surf})$. Practically the whole of the energy deposited on the surface is used in the evaporation of atoms: estimates show that other channels for the removal of energy from the surface are unimportant. If the distribution of the velocities of the evaporating atoms is semi-Maxwellian near the surface, the following relationship is obtained for the energy balance near the surface:

$$P = (\Delta H + 2T_{\rm surf})j(T_{\rm surf}) , \qquad (2.1)$$

where P is the energy flux absorbed by the surface; ΔH is the binding energy of an atom in a solid at T_{surf} , i.e. the binding energy per atom in a macroscopic system; $\Delta H + 2T_{surf}$ is the average energy lost in the evaporation of one atom.

We shall find the value of $j(T_{surf})$ from the condition that in equilibrium near the surface the fluxes of the atoms evaporating from the surface and of the atoms condensing on it are equal. Let us introduce a parameter ξ , known as the accommodation coefficient, and representing the probability that an atom colliding with the surface sticks to it. Then, the condition for a vapour equilibrium near the surface gives

$$j(T_{\rm surf}) = \frac{1}{4} \xi N_{\rm sat}(T_{\rm surf}) \left(\frac{8T_{\rm surf}}{\pi m}\right)^{1/2} , \qquad (2.2)$$

where $N_{\text{sat}}(T_{\text{surf}})$ is the number density of atoms at the saturated vapour pressure and *m* is the mass of an atom. Eqns (2.1) and (2.2) represent the energy balance at the surface and they govern the surface temperature at a given absorbed energy flux. The density of the evaporating atoms near the surface is $\xi N_{\text{sat}}(T_{\text{surf}})$.

Near the surface, as long as the distance from the surface does not exceed the mean free path of atoms, the distribution of the velocity of the evaporating atoms is semi-Maxwellian since these atoms move away from the surface. At larger distances the flux of atoms forms a gasdynamic beam. The process of formation of such a beam has been studied [80-82] and the results of these studies will be used here. The beam parameters depend on the gas pressure in the phase which the evaporating atoms enter. Let us consider the limiting case when the pressure of the evaporating atoms in a beam is high compared with the buffer gas pressure. Then the evaporating atoms move at the velocity of sound and the beam parameters correspond

to the balance of the flux of atoms and energy near the surface and in the gasdynamic beam:

$$j = uN_{\rm b}, \quad 2T_{\rm surf} = \frac{1}{2}Mu^2 + \frac{5}{2}T_{\rm b} , \qquad (2.3)$$

where N_b is the density of atoms in the beam; T_b is the beam temperature; $u = (\gamma T_b/M)^{1/2}$ is the velocity of sound; γ is the ratio of the specific heat at a constant pressure and volume, which is 5/3 for an atomic gas. These expressions make it possible to establish a simple realtionship between the parameters of the evaporating atomic gas before and after the formation of an atomic beam:

$$T_{\rm b} = 0.69T_{\rm surf}, \quad N_{\rm b} = 0.25N_{\rm surf} \;.$$
 (2.4)

Eqn (2.3) gives the parameters of the resultant beam. By way of demonstration, let us consider an example which will be useful later in dealing with the various processes occurring in the system and thus provide an illustration of a complete physical picture of the effect in question. Our example will be, here and later, a plasma formed by laser irradiation of a copper surface. Other examples of the formation of atomic beams will also be considered. The following parameters of the interaction of laser radiation with a surface will be assumed: the efficiency of utilisation of the laser radiation energy in the evaporation of atoms (i.e. the fraction of the laser radiation energy expended in the evaporation process) is 0.3 and the probability of attachment of copper atoms to the surface after coming into contact with it is $\xi = 0.2$. Table 1 gives the parameters of such a copper plasma near the surface for certain characteristic values of the energy fluxes (power densities) relevant to the investigated regime. The saturated copper vapour pressure is the result of extrapolation [83, 84] to higher temperatures. In the notation used the subscript 'surf' identifies the parameters of the evaporating plasma near the surface, the index 'b' is used for the plasma parameters in the beam, and $N_{e,b}$ is the equilibrium electron density in the resultant beam.

Table 1. Parameters of a copper plasma formed by laser irradiation of a copper surface, calculated assuming that 30% of the laser radiation energy is absorbed by the surface and that the probability of attachment of copper atoms to the surface is $\xi = 0.2$.

	Radiation energy flux/W cm ^{-1}			
	10 ⁷	3×10^{6}	10 ⁶	
$\overline{T_{\rm surf}/\rm K}$	7340	5440	4410	
$N_{\rm surf}/10^{19}{\rm cm}^{-3}$	11	4.1	1.6	
P _{surf} /bar	110	30	9.4	
$T_{\rm b}/{\rm K}$	4910	3640	2950	
$N_{\rm b}/10^{19}{\rm cm}^{-3}$	2.8	1.0	0.4	
$P_{\rm b}/{\rm bar}$	19	5.0	1.6	
$N_{\rm e,b}/10^{14}{\rm cm}^{-3}$	160	2.1	0.1	

We shall use this example to demonstrate the results of an analysis of various aspects of the investigated phenomena. We shall therefore refine the conditions for the process being analysed. We shall assume that the laser radiation power is 10 kW and that focusing of this radiation can create any energy flux (power density) in the investigated range $10^6 - 10^7$ W cm⁻². The characteristic plasma propagation time is of the order of 10^{-5} s and the propagation

[†]Throughout this paper the temperature will be given in energy units, which makes it possible to omit the frequently used factor for conversion of the energy and temperature units.

process is quasisteady. This means that the duration of a laser radiation pulse exceeds the plasma evolution time of $\sim 10^{-5}$ s. Therefore, the laser used may be pulsed or pulse-periodic, and the laser parameters given here are readily attainable. For example, if a laser generates pulses of 10^{-3} s duration, the energy per pulse has to be 10 J. The wavelength of the laser radiation is not of fundamental importance and it is allowed for by introduction of the coefficient of absorption of the radiation on the target surface.

2.2 Loss of ionisation equilibrium in an expanding plasma A weakly ionised plasma beam formed in this way moves away from the surface and expands, so that it cools. Depending on the conditions during the formation of this beam, and also on the nozzle and skimmer parameters used in the beam sources, the angle between the boundary of the beam and the symmetry axis of the beam cone is assumed to be $\alpha = 5^{\circ} - 15^{\circ}$ [85]. In future estimates we shall assume that $\alpha = 10^{\circ}$. The law of variation of the density *j* of the flux of atoms at a distance *x* from the surface subjected to laser radiation is

$$j(x) = j(0)(1 + x \tan \alpha R_0^{-1})^2$$
,

where R_0 is the radius of the heated spot on the surface. Bearing in mind that the gas expansion is adiabatic, we can find the nature of changes in its temperature and density as the beam moves away from the evaporating surface. If we assume that the evaporating material consists mainly of atoms, we find that the relationship between the density of atoms and temperature in an adiabatic process is [38, 86– 88]

$$N \propto T^{3/2}$$

Since the flux density of atoms is $j \propto N \overline{\nu} \propto T^2$ ($\overline{\nu}$ is the directional velocity of the beam), it follows from the above expression for the flux in an atomic beam that the beam temperature varies with distance away from the evaporating surface:

$$T = T_0 (1 + x \tan \alpha R_0^{-1})^{-1} .$$
(2.5)

The evolution of the electron density during expansion of a weakly ionised plasma in space is of fundamental importance. The later stages of plasma expansion involve conversion of electrons into negative ions, which together with positive ions become the condensation nuclei for the evaporated material. If electrons recombine with ions, the subsequent condensation is impossible. Therefore, we shall analyse later the nature of the evolution of the electron component in the course of expansion of a weakly ionised plasma.

At high temperatures of a weakly ionised gas the rate of establishing of an ionisation equilibrium is relatively rapid, so that the electron density is given by the Saha formula and depends exponentially on the plasma temperature. Since the frequency representing the establishment of an ionisation equilibrium is proportional to the electron density, this density falls steeply when temperature is lowered. At some temperature the rate at which ionisation equilibrium is established becomes comparable with the plasma expansion rate and at lower temperatures the ionisation equilibrium is lost. My asymptotic theory [41-43, 89] of the evolution of the electron component will be presented on the assumption

that the ionisation equilibrium is maintained by the processes

$$e + A \xrightarrow{\longrightarrow} 2e + A^+$$
, (2.6)

where e, A, and A^+ are an electron, an atom, and an ion, respectively. The three-body recombination rate constant at low temperatures is [90]

$$K(T) = CT^{-9/2} ,$$

where $C = 2.0 \times 10^{-8} \text{ cm}^6 \text{ K}^{9/2} \text{ s}^{-1}$ [91].

The characteristic time of attaining ionisation equilibrium is $\tau_e \propto (KN_e^2)^{-1}$. It follows from Eqn (2.5) that the expansion-cooling time of the plasma is

$$\tau_T = \left(\frac{\mathrm{d}\ln T}{\mathrm{d}l}\right)^{-1} = R\left(u\,\tan\alpha\right)^{-1} \,, \tag{2.7}$$

where R is the radius of the plasma beam at a given distance from the surface. Obviously, the ionisation equilibrium is lost when the time τ_e for the establishment of this equilibrium becomes comparable with the time of a change in the equilibrium plasma. Here, $N_s \propto \exp(-J/2T)$ is the equilibrium electron density given by the Saha formula, where J is the ionisation potential of the atoms. We can see that $d \ln N_e/dt = -(J/T)/\tau_T$, so that the ionisation equilibrium is lost at temperatures such that

$$\tau_{\rm e} \sim \tau_T \frac{T}{J} \ . \tag{2.8}$$

At lower temperatures the ionisation of atoms by electron impact can be ignored and, in accordance with Eqn (2.6), the equation for the balance of the electron density is (if allowance is made for the quasineutrality of the plasma)

$$\frac{\mathrm{d}N_{\mathrm{e}}}{\mathrm{d}t} = -KN_{\mathrm{e}}^3 \ .$$

Its solution is

$$N_{\rm e} = \left(\int_{t_0}^t K \,\mathrm{d}t\right)^{-1/2} \,, \tag{2.9}$$

where t_0 is the moment at which the condition of Eqn (2.8) is satisfied.

The lower limit in Eqn (2.9) can be found more accurately from the balance equation for the electron density

$$\frac{dN_{\rm e}}{dt} = KN_{\rm e} (N_{\rm s}^2 - N_{\rm e}^2) , \qquad (2.10)$$

where N_s is the equilibrium electron density given by the Saha formula. When temperature is varied slowly, this equation yields $N_e = N_s$, i.e. it corresponds to the ionisation equilibrium in this system. When temperature is varied more rapidly, we have $N_s \ll N_e$, so that the ionisation of atoms can be ignored and the solution of the above equation is given by Eqn (2.9).

Let us now find the asymptotic solution of Eqn (2.10). Let us assume that the transition region is fairly narrow and that in this region we have K = const and either $N_s \propto \exp(-\alpha t/2)$, where $\alpha = 2J/(T\tau_T)$, or $N_s \propto \exp(-J/2T)$. Then, Eqn (2.10) becomes

$$\frac{\mathrm{d}N_{\mathrm{e}}}{\mathrm{d}t} = KN_{\mathrm{e}} \left[N_{\mathrm{s}}^{2}(0) \exp(-\alpha t) - N_{\mathrm{e}}^{2} \right] \; .$$

Its solution at high values of t is given by the expression

$$N_{\rm e}^{-2} = 2K\alpha^{-1} \left\{ \alpha t - \ln[2KN_{\rm s}^2(0)\alpha^{-1}] - C \right\} , \qquad (2.11)$$

where C = 0.577 is the Euler constant. We can see that this solution is independent of the selected initial moment. A comparison with Eqn (2.9) allows us to find t_0 :

$$\alpha t_0 = C + \ln \left[2KN_s^2(0) \alpha^{-1} \right] .$$

At this moment the following relationship is obeyed:

$$KN_s^2(t_0) = \frac{1}{2}\alpha \exp(-C) = \frac{0.28J}{T\tau_T}$$
 (2.12)

This relationship is identical with Eqn (2.8), but the initial moment is found more accurately.

We shall now introduce in Eqn (2.9) the temperature dependence of the rate constant of the process for wide ranges of variation of temperature and time. It follows from Eqn (2.5) that $T \propto 1/R$, where *R* is the beam radius at a given point. Moreover, $dR/dt \propto u \propto T^{1/2}$ and hence $\tau_T = (d \ln T/dt)^{-1} \propto T^{-3/2}$. This dependence allows us to derive the following expression from Eqn (2.9) if Eqn (2.12) is taken into account:

$$\frac{1}{N_{\rm e}^2} = \frac{1}{3} K(T) \tau_{\rm ex}(T) \left[1 - \left(\frac{T}{T_0}\right)^6 \right]$$
$$= 0.093 J \left[\left(\frac{T_0}{T} - 1\right)^6 \right] \left[N_{\rm s}^2(T_0) T_0 \right]^{-1}, \qquad (2.13)$$

where the temperature T_0 corresponds to the time t_0 .

The results obtained allow us to describe the evolution of the electron component of a plasma when it expands in space. We shall demonstrate the results by considering the example of a laser copper plasma mentioned earlier (Table 1). Its parameters relating to the evolution of electrons and atoms during the initial stage of the plasma beam expansion, when condensation of the evaporating material is unimportant, are presented in Table 2. The temperature T_0 given by Eqn (2.12) is the limit of the ionisation equilibrium. For a given temperature dependence of the density of atoms N(T) the temperature T_c is defined by

$$N(T_{\rm c}) = N_{\rm sat}(T_{\rm c}) , \qquad (2.14)$$

where $N_{\text{sat}}(T)$ is the number density of the saturated vapour at a given temperature. At lower temperatures the

Table 2. Parameters of the evolution of a laser copper plasma.

	Radiation flux/W cm^{-2}			
	10 ⁷	3×10^{6}	10 ⁶	
Irradiation spot radius/mm	0.18	0.33	0.56	
$T_{\rm e}/{\rm K}$	3740	3910	4100	
$\tau_T(T_{\rm c})/10^{-6}{\rm s}$	0.96	1.4	2.6	
T _c /K	3270	2720	2360	
$N_{\rm c}/10^{18}{\rm cm}^{-3}$	15	6.4	2.9	
$N_{\rm c}(T_{\rm c})/10^{14}{\rm cm}^{-3}$	12	5.8	3.0	
$N_{\rm e}(T_{\rm c})[N_{\rm s}(T_{\rm c})]^{-1}$	6.8	67	600	
$T_{\rm a}/{\rm K}$	2990	2670	2400	
T _r /K	2740	2450	2250	
$Y(T_{\rm a})$	2.0	1.9	1.6	
$N_{\rm i}(0)/10^{14}{\rm cm}^{-3}$	2.0	1.0	0.9	
$N_{\rm i}(\infty)/10^{13}{\rm cm}^{-3}$	2.7	3.3	3.5	

condensation of atoms may occur on the copper surface, which is at the same temperature.

The following notation is used in Table 2: N_e is the electron number density, N_s is the equilibrium density of electrons. We can see that at T_c the ionisation equilibrium is strongly violated, which accelerates the process of condensation during the subsequent cooling of the plasma if ions act as the condensation nuclei of the supersaturated vapour.

2.3 Electron decay and formation of negative ions

Electrons and ions are converted in the investigated expanding plasma into cluster ions and become the condensation nuclei which collect the evaporating material. Therefore, the stage of conversion of electrons into negative ions and of positive atomic ions into molecular ions is important in the evolution of the plasma. The following processes occurring during this stage are of interest:

$$e + 2A \overrightarrow{\longrightarrow} A^- + A$$
, (2.15)

$$2A + A^+ \overleftrightarrow{} A_2^+ + A , \qquad (2.16)$$

$$\mathbf{e} + \mathbf{A}_2^+ \overrightarrow{\longrightarrow} \mathbf{A} + \mathbf{A}^* \quad . \tag{2.17}$$

Electrons decay in two channels, described by Eqns (2.15) and (2.17), and the subsequent evolution of the plasma depends on the competition between these channels. In particular, in the limiting case when electrons decay by dissociative recombination [Eqn (2.15)], the density of ions during the next stage of the evolution of the system becomes low and the evaporated material does not condense.

We shall now consider the case when the times for the establishment of an equilibrium given by Eqns (2.15) and (2.17) are much shorter than the plasma cooling time. This is true in particular of the evolution of a copper plasma, considered here by way of example. Then at any given plasma temperature there is a thermodynamic equilibrium for the processes described by Eqns (2.15) and (2.17), so that the densities of electrons N_e and of negative ions $[A^-]$, and the densities of atomic $[A^+]$ and molecular $[A_2^+]$ ions are related by the Saha formula:

$$\frac{N_{\rm e}}{[{\rm A}^-]} = a \exp\left(-\frac{EA}{T}\right) = X(T) ,$$

$$\frac{[{\rm A}^+]}{[{\rm A}_2^+]} = b \exp\left(-\frac{D}{T}\right) = Y(T) .$$
(2.18)

Here, EA is the energy representing the binding of an electron to a negative ion; D is the dissociation energy of a positive molecular ion; a and b are numerical coefficients which depend weakly (in accordance with a power law) on the plasma temperature T; we shall ignore this dependence in future because the range of temperatures corresponding to the stage under consideration is relatively narrow.

In view of the plasma quasineutrality, we shall introduce the density of positively and negatively charged particles:

$$N_{\rm i} = N_{\rm e} + [{\rm A}^-] = [{\rm A}^+] + [{\rm A}_2^+]$$
.

We can see that the fraction of electrons, relative to the total density of charged particles at a given temperature, is X/(1+X), and the fraction of positive atomic atoms is Y/(1+Y). Dissociative recombination results in an irreversible loss of the charge, since the trapping of

electrons by atoms conserves the total density of charged particles and changes only their type. The balance equation for the electron number density is

$$\frac{\mathrm{d}N_{\mathrm{e}}}{\mathrm{d}t} = -\alpha N_{\mathrm{e}}[\mathrm{A}_{2}^{+}] + \left(\frac{\mathrm{d}N_{\mathrm{e}}}{\mathrm{d}t}\right)_{\mathrm{at}}$$

where α is the coefficient of dissociative recombination of electrons and molecular ions. The second term allows for the transfer of electrons to negative ions. This balance equation can be rewritten for the total density of charged particles:

$$\frac{\mathrm{d}N_{\rm i}}{\mathrm{d}t} = -\alpha N_{\rm e}[{\rm A}_2^+] = -\frac{\alpha N_{\rm i}^2 X}{(1+X)(1+Y)^{-1}} \ .$$

The rate of change of the variable X, defined by

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{X}{\tau_T} \frac{EA}{T} \; ,$$

changes the above equation to

$$\frac{\mathrm{d}N_{\rm i}}{\mathrm{d}X} = -\frac{VN_{\rm i}^2}{(1+X)(1+Y)} ,$$

where $V = \alpha \tau_{ex} T / EA$. The solution of this equation is

$$N_{i}^{-1} = (N_{i}(\infty))^{-1} + V \int dX \frac{1}{(1+X)(1+Y)}$$

Hence it follows that as the system passes through the recombination region, the number density of charged particles becomes

$$N_{i}(t=\infty) = \frac{N_{i}(t=0)}{1 + VJN_{i}(t=0)} , \qquad (2.19)$$

where

$$J = \int_0^\infty \, \mathrm{d}X \, \frac{1}{(1+X)(1+Y)} \; .$$

The required integral is J = 1, if X = Y. The parameters X and Y vary from zero to infinity. Temperatures T_a and T_r will be introduced on the basis of the following relationships:

$$X(T_{\rm a}) = 1, \quad Y(T_{\rm r}) = 1$$
, (2.20)

which represent the temperature range where the investigated processes occur. We have $Y = Y(T_a)X^k$, where k = D/EA. The required integral is readily calculated by numerical methods. In the case of a copper plasma, it amounts to J = 0.5 - 0.6.

Table 2 lists some of the laser copper plasma parameters related to the processes under consideration. Since no information is available on the recombination of molecular copper ions, the coefficients of dissociative recombination of electrons with Ar_2^+ argon ions [92, 93] are used. Therefore, the data on the evolution of the density of charged particles obtained for this range of parameters are approximate.

It is worth noting the following in an analysis of the data in Table 2. The range of temperatures where the electron component decays is located below T_c , at which condensation of a vapour on a flat surface becomes possible. Therefore, the condensation of a vapour in the bulk, accompanied by the formation of clusters, occurs at even lower temperatures. Moreover, the dissociative recombination of electrons and molecular ions may result in the loss of a significant proportion of the charged particles.

2.4 Mutual neutralisation of positive and negative ions

Since the condensation rate is proportional to the density of ions which act as the condensation nuclei, it follows that the processes resulting in the loss of ions are important in the condensation stage. We shall now consider the processes involving charge exchange from positive to negative ions, resulting in mutual neutralisation of the ions.

We shall consider the process

$$A_n^- + A_m^+ \longrightarrow A_n + A_m \quad . \tag{2.21}$$

As a result of it an electron is transferred from a negative cluster to the field of a positively charged cluster. We shall consider this process on the basis of an asymptotic model [94] corresponding to a low energy of binding of an electron to a negative ion. The electron transfer probability is then a sharp function of the distance of closest approach between the clusters. At low collision energies the cross section of the process (2.21) is

$$\sigma = \pi \frac{e^2}{\varepsilon} R_0, \quad R_0 \ll \frac{e^2}{\varepsilon} , \qquad (2.22)$$

where e is the electron charge; ε is the collision energy; R_0 is the distance of closest approach at which the probability of charge exchange is of the order of unity.

An analysis in Ref. [94] shows that at low values of $\gamma = (2m_c EA/\hbar^2)^{1/2}$ (*EA* is the energy of affinity of a cluster to an electron, m_e is the electron mass, and \hbar is the Planck constant) the product $R_0\gamma$ depends weakly on the other parameters of the problem. This is because the transition in question occurs in the tail of the function of an electron belonging to a negative ion, which falls exponentially as $e^{-r\gamma}$ with the distance r from a cluster. For this reason the product $R_0\gamma \approx 6$ [94]. This value and Eqn (2.22) give the following expression for the mutual neutralisation rate constant if averaging is carried out over the Maxwellian cluster velocity distribution:

$$k \approx \frac{30 e^2}{(\mu T)^{1/2} \gamma} ,$$
 (2.23)

where T is the temperature and μ is the reduced mass of a cluster.

The reduced mass of a cluster consisting of q_1 and q_2 atoms is

$$\mu = m \frac{q_2 + q_1}{q_1 q_2} , \qquad (2.24)$$

where m is the mass of one atom. This gives us the balance equation for the density of charged clusters:

$$\frac{\mathrm{d}N_{+}}{\mathrm{d}t} = -\frac{30e^{2}}{\gamma(mT)^{1/2}} \left\langle \left(\frac{q_{1}+q_{2}}{q_{1}q_{2}}\right)^{1/2} \right\rangle N_{+}^{2} \quad (2.25)$$

Here, N_+ is the number density of charged clusters, which allows for the quasineutrality of the system and the averaging corresponds to a given distribution of the cluster sizes. The simplest form of the distribution of clusters in terms of the number of atoms q in a cluster is

$$f(q) = \frac{\exp(-q/\bar{q})}{\bar{q}} , \qquad (2.26)$$

where \overline{q} is the average number of atoms in a cluster. This distribution function can be used to transform the balance equation (2.25) to

$$\frac{\mathrm{d}N_+}{\mathrm{d}t} = -k_{\rm r}N_+^2\bar{q}^{-1/2} , \qquad (2.27)$$

where $k_{\rm r} = 84e^2/[\gamma(mT)^{1/2}]$.

The expression for the neutralisation rate constant is valid provided the temperature is low and the clusters are not too large. The distance between clusters, which has to be traversed by an electron from the field of a neutral cluster to one of a positive cluster, must exceed the cluster size.

We shall now give relevant estimates for copper clusters. The energy of affinity of a copper atom to an electron is EA = 1.23 eV [95, 96], i.e. $\gamma = 0.3/a_0$, where a_0 is the Bohr radius. The work function of copper, i.e. the energy of affinity of an electron to an infinitely large cluster is 4.4 eV [97], i.e. $\gamma = 0.57/a_0$. For clusters with q < 30 the electron affinity energy is less than 3 eV [98]. We shall therefore assume that $\gamma = 0.4/a_0$, so that the distance between clusters governing the cross section for mutual neutralisation of clusters is $R_0 \approx 15a_0$. The number of atoms contained in a cluster of radius R_0 is $q = 4\pi R_0^3 \rho/3m$, where m is the mass of an atom and ρ is the density of the condensed material. For copper this quantity amounts to $q \sim 100$ which is the limit above which Eqn (2.23) is invalid. In the case of copper the parameter k_0 is $k_{\rm r} \approx 4 \times 10^{-8} \, {\rm cm}^3 \, {\rm s}^{-1}$ at temperatures from which condensation begins.

For large clusters the distance of closest approach, corresponding to the mutual neutralisation of clusters, is equal to the sum of the radii. Then Eqn (2.22) yields the cross section for mutual neutralisation of clusters:

$$\sigma = \pi \frac{e^2}{\varepsilon} (r_1 + r_2), \quad r_1, r_2 \ll \frac{e^2}{\varepsilon} , \qquad (2.28)$$

where r_1 and r_2 are the cluster radii. Averaging over the Maxwellian distribution of clusters yields the rate constant of the process

$$k = \left(\frac{8\pi}{T\mu}\right)^{1/2} e^2(r_1 + r_2) \quad . \tag{2.29}$$

Averaging this expression with the distribution function (2.26) of clusters in terms of the numbers of atoms in them, we obtain

$$k = \left(\frac{8\pi}{T\mu}\right)^{1/2} \left(\frac{3m}{4\pi\rho}\right)^{1/3} \left\langle \left(\frac{q_1+q_2}{q_1q_2}\right)^{1/2} (q_1^{1/3}+q_2^{1/3}) \right\rangle$$
$$\cong 13 \ e^2 T^{-1/2} m^{-1/6} \rho^{-1/3} \bar{q}^{-1/6} , \qquad (2.30)$$

where *m* is the mass of an atom and ρ is the density of the condensed material. We can represent Eqn (2.30) in the form

$$k = k_{\rm rec} \bar{q}^{-1/6} ,$$

where

$$k_{\rm rec} = 13e^2 T^{-1/2} m^{-1/6} \rho^{-1/3} . \qquad (2.31)$$

The balance equation for the density of cluster ions is then

$$\frac{\mathrm{d}N_{+}}{\mathrm{d}t} = -k_{\mathrm{rec}}N_{+}^{2}\bar{q}^{-1/6} \quad . \tag{2.32}$$

Here, N_+ and N_- are the number densities of positive and negative cluster ions; $N_+ = N_-$.

In the derivation of the balance equation (2.32) it is assumed that the bending of the paths because of the Coulomb interaction of ions significantly alters the distance of closest approach in their collisions [Eqn (2.22)]. In general, the expressions for the cross section of the process in question becomes, instead of Eqn (2.22),

$$\sigma = \pi e^2 \frac{R_0}{\varepsilon} + \pi R_0^2 \quad . \tag{2.33}$$

According to the liquid drop model of clusters the effective distance of closest approach is equal to the sum of the radii of the colliding ions $R_0 = r_1 + r_2$, where r_1 and r_2 are the radii of the colliding clusters. The coagulation rate constant is then

$$k_{\text{coag}} = \langle [8T(\pi\mu)^{-1}]^{1/2}\pi(r_1 + r_2)^2 \rangle = 13.5 \, T^{1/2} m^{1/6} \rho^{-2/3} \,.$$
(2.34)

Replacement of Eqn (2.22) with Eqn (2.33) for the cross section of the process modifies the balance equation (2.31) to

$$\frac{\mathrm{d}N_+}{\mathrm{d}t} = -(k_{\rm rec}\,\bar{q}^{-1/6} + k_{\rm coag}\,\bar{q}^{1/6})N_+^2 \ . \tag{2.35}$$

The values of the required rate constants at a temperature $T_{\rm e}$, at which the pressure of a weakly ionised plasma is equal to the saturated vapour pressure at a given temperature, are listed in Table 3 for the investigated case of a laser copper plasma. They make it possible to analyse the influence of the process of charge exchange from a negative to a positive cluster ion during cluster growth on the nature of neutralisation in the system. This should be analysed together with the growth of charge clusters.

 Table 3. Parameters and rate constants of processes in an expanding copper plasma.

	Radiation flux/W cm ^{-2}			
	10 ⁶	3×10^{6}	10 ⁷	
$T_{\rm c}/{\rm K}$	3270	2720	2360	
$k_{\rm r}/10^{-8}{\rm cm}^3{\rm s}^{-1}$	3.7	4.1	4.4	
$k_{\rm rec}/10^{-8}{\rm cm}^3{\rm s}^{-1}$	1.0	1.1	1.2	
$k_{\rm coag}/10^{-10} {\rm ~cm}^3 {\rm ~s}^{-1}$	4.6	4.2	3.9	
$k_0/10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1}$	6.6	6.0	5.6	
$s = N_{\rm m} (N + N_{\rm m})^{-1}$	0.23	0.33	0.44	
$q_{ m cr}$	340	590	900	

It therefore follows that the evolution of an expanding weakly ionised gas, which is evaporated from the surface or is formed in some other way, consists of a series of consecutive processes involving charged particles. The relationship between the times of these processes and the motion of a gas create specific conditions for the evolution of the system, so that its state differs considerably from the state of thermodynamic equilibrium. The survival of charged particles in such a system is of fundamental importance for the condensation of the gas at the next stage of expansion because ions subsequently become the condensation nuclei.

3. Large clusters in a hot gas

3.1 Equilibrium distribution of clusters

In the course of its expansion a weakly ionised gas reaches a state with parameters such that its pressure becomes comparable with the saturated vapour pressure at a given temperature. Then, the condensation associated with the formation and growth of clusters may begin in the expanding gas and charged particles play the role of the condensa-tion nuclei. The temperature at which this begins is denoted by $T_{\rm c}$. In reality, the condensation process occurs at lower temperatures. In particular, Table 3 gives the fraction s of the molecules in our copper plasma at the temperature $T_{\rm c}$ when atoms and molecules are in a thermodynamic equilibrium. It follows from this table that the average number of atoms in molecules and clusters does not differ greatly from unity. Moreover, we recall that at the temperature T_r listed in Table 2 the densities of atomic and molecular ions in the system are the same. Thus, even under equilibrium conditions the transition from an atomic vapour to one containing clusters occurs at temperatures well below $T_{\rm c}$.

Another feature of the condensation process is associated with the instability of neutral clusters until the number of atoms in them becomes large. It follows from the classical theory of condensation [36-40] and the drop model of clusters that there is a critical cluster radius or a critical number of atoms in a cluster corresponding to the minimum value of the cluster size distribution function under thermodynamic equilibrium conditions. The equilibrium distribution function of the clusters will be determined in terms of the numbers of atoms in them on the basis of the following assumptions. First, we shall adopt the liquid drop model for clusters and assume that the properties of the surface layer of a cluster are the same as those of a macroscopic system. Second, we shall postulate that an equilibrium results from the attachment or evaporation of single atoms.

The similarity of the surface of such a cluster to a macroscopic surface can be used to consider first the attachment and evaporation fluxes for a macroscopic surface. The attachment flux of atoms from the gaseous phase to the macroscopic surface is

$$j_{\text{att}} = [T(2\pi m)^{-1}]^{1/2} N\xi , \qquad (3.1)$$

where the first factor represents the average component of the velocity of atoms normal to the surface; *m* is the mass of an atom; *N* is the number density of atoms; ξ is the probability of attachment to the surface of an atom colliding with it. The flux of evaporated atoms is

$$j_{\rm ev} = A \, \exp\left(-\frac{\varepsilon_{\rm sub}}{T}\right) \,,$$
 (3.2)

where the parameter A depends weakly on temperature and is governed by the surface properties; ε_{sub} is the binding energy of a surface atom, which is identical with the sublimation energy of a macroscopic system of bound atoms. When the atom number density N_{sat} is equal to the saturated vapour density at a given temperature, the attachment and evaporation fluxes become identical [see Eqn (2.2)], i.e.

$$\dot{J}_{\text{att}} = [T(2\pi m)^{-1}]^{1/2} N_{\text{sat}}(T) \xi$$

In the case of clusters which can be modelled by a liquid drop we have the same expression (3.1) for the flux of atoms which become attached to the surface, whereas in the expression for the flux of evaporating atoms (3.2) we have to use the energy ε_q of binding of a surface atom to a cluster, which depends on the number of atoms q in a cluster. Eqn (3.2) for a cluster then becomes

$$j_{\rm ev} = A \exp\left(-\frac{\varepsilon_q}{T}\right)$$

= $[T(2\pi m)^{-1}]^{1/2} N_{\rm sat}(T) \xi \exp\left(-\frac{\varepsilon_q - \varepsilon_{\rm sub}}{T}\right).$ (3.3)

Under the conditions of thermodynamic equilibrium between clusters containing q-1 and q atoms, the frequencies of cluster dissociation and formation are equal, i.e.

$$N_q j_{\rm ev} = N_{q-1} j_{\rm att}$$
, (3.4)

where N_q is the density of clusters containing q atoms. Hence, we obtain

$$N_{q-1} \frac{N}{N_q} = N_{\text{sat}} \exp\left(-\frac{\varepsilon_q - \varepsilon_{\text{sub}}}{T}\right) .$$
(3.5)

The structure of this relationship is identical with the Saha distribution. It in fact corresponds to the equilibrium

$$\mathbf{A}_{q-1} + \mathbf{A} \overrightarrow{\longrightarrow} \mathbf{A}_q \quad , \tag{3.6}$$

where A is an atom, and in this respect it is a full analogue of the Saha distribution for high values of q. Therefore, the left-hand side of Eqn (3.5) corresponds to any values of qin the case when the thermodynamic equilibrium is maintained by the attachment of individual atoms. The right-hand side of this relationship corresponds to high values of q. It is interesting to consider how this relationship works at low values of q beyond the limit of its validity. This is illustrated in Table 4, which gives the quantity

$$f = \frac{N^2}{N_{\rm m}N_{\rm sat}(T)} \exp\left(\frac{D - \varepsilon_{\rm sub}}{T}\right) , \qquad (3.7)$$

where $N_{\rm m}$ is the number density of diatomic molecules and D is the dissociation energy of a diatomic molecule. The quantity f is the ratio of the left-hand part of the Saha distribution in the case of an equilibrium between atoms and diatomic molecules to the expression on the right of Eqn (3.5), which applies to large clusters. This ratio would be equal to unity if Eqn (3.5) were identical with the Saha distribution for q = 2. Table 4 gives the saturated vapour pressure in torr at a given temperature. The parameters of the copper and silver molecules are taken from [100] and [101], respectively.

Table 4.

	<i>P</i> _{sat} /Torr	1	10	100	1000
Ag	$T_{\rm sat}/{\rm K}$	1634	1896	2258	2792
Cu	$T_{\rm sat}/{ m K}$	1.0 1596 4.4	1820 4.1	2114 3.9	2525 3.5

We shall introduce the degree of supersaturation of the vapour:

$$S = \frac{N}{N_{\text{sat}}(T)} . \tag{3.8}$$

Then, Eqn (3.5) becomes [102]

$$\frac{N_q}{N_{q-1}} = S \, \exp\left(\frac{\varepsilon_q - \varepsilon_{\rm sub}}{T}\right) \,. \tag{3.9}$$

Hence we can obtain the critical size of a cluster q_{cr} , which corresponds to the minimum number density of the clusters:

$$S \exp\left(\frac{\varepsilon_q - \varepsilon_{sub}}{T}\right) = 1, \quad S > 1$$
 (3.10)

We shall find the critical size of a drop in the classical theory of homogeneous condensation in [36-40] in which a cluster is modelled by a liquid drop. Then the number q of atoms in a cluster is related to the cluster radius r by

$$q = \frac{4\pi\rho r^3}{3m} , \qquad (3.11)$$

where ρ is the density of the liquid, *m* is the mass of an atom, and the total binding energy of atoms in a cluster is

$$E_q = \varepsilon_{\rm sub} q - 4\pi r^2 \alpha , \qquad (3.12)$$

where α is the surface tension of the liquid. Hence, the binding energy of a surface atom in a cluster is

$$\varepsilon_q = \frac{\mathrm{d}E_q}{\mathrm{d}q} = \varepsilon_{\mathrm{sub}} - \alpha [32\pi m (3\rho q)^{-1}]^{1/3}$$

Substitution of this expression into Eqn (3.10) gives the critical number of atoms in a cluster,

$$q_{\rm cr} = 32\pi m^2 \left\{ 3\rho^2 [\alpha (T \ln S)^{-1}]^3 \right\}^{-1}, \qquad (3.13)$$

or the critical radius of a cluster (drop),

$$r_{\rm cr} = \frac{2\alpha m}{\rho T \,\ln\,S} \ . \tag{3.14}$$

These expressions are obtained from the classical theory of homogeneous condensation. The critical radius corresponds to the minimum equilibrium density of clusters. This means that in the course of the evolution of a test cluster it continues to grow when it reaches the critical size. However, if the size of a cluster is less than critical, its subsequent evolution involves evaporation. The critical size of a cluster is fairly large. Table 3 gives the values of q_{cr} for a copper plasma near the temperature T_c and for the degree of supersaturation of the vapour S = 2.

Since $\varepsilon_{sub} \ge T$, the critical number of atoms in a cluster is fairly large. In particular, for the copper plasma in question expanding in space we have $q_{cr} \sim 10^3$ (Table 3). Large values of q_{cr} imply that the condensation in a real expanding plasma can occur only at ions acting as the condensation nuclei. Consequently, only charged clusters grow in an expanding plasma. Neutral clusters can form in the system only by coagulation of large charged clusters.

Eqns (3.5) and (3.9) make it possible to relate the equilibrium density of clusters at a given temperature to the number density of atoms. This relationship can be established with exponential precision and is given by

$$N_q = NS^q \exp\left(-\frac{E_{\rm sur}(q)}{T}\right) , \qquad (3.15)$$

where

$$E_{
m surf}(q) = \sum_{k=1}^{q} (\varepsilon_{
m sub} - \varepsilon_k)$$

is the surface energy of a cluster.

If E_{surf} is expanded in powers of $1/q^{1/3}$ and only the first term of the expansion is retained, the result is accurate to within $\exp(\text{const} \times q^{1/3})$. If two terms of the expansion are included, the precision is governed by a factor independent

of q and is much poorer than in the case illustrated in Table 4. The preexponential factor can be found more accurately if full information on the systems of bound states is available for all values of q.

It is worth noting the following circumstance: in accordance with Eqn (3.5), at high values $q > q_{cr}$ the number density of clusters increases with the number of atoms in a cluster; i.e. under thermodynamic equilibrium conditions in the system, the clusters containing a small number of atoms (including free atoms) do not contribute to the total mass of bound atoms.

However, the reality is different. If we use the number density of atoms to determine the number density of clusters, we implicitly assume that a complete thermodynamic equilibrium for clusters, described by Eqn (3.15), cannot be achieved at high values of q. This means that the evolution times of a system containing atoms and clusters, when the process begins from a system of free atoms, are short compared with the typical times of growth of large neutral clusters. The relationship between the number densities of clusters of similar dimensions, corresponding to Eqns (3.5) and (3.9), is valid because the time for the establishment of equilibrium given by Eqn (3.6) is relatively short and does not exceed the time for the establishment of an equilibrium between atoms and diatomic molecules. These are the conditions under which the distributions (3.5), (3.9), and (3.15) are valid for large but finite clusters.

3.2 Heat regimes during expansion of a condensing vapour

The main special feature of the condensation process is the nature of removal of the energy released in condensation. This energy is relatively high. It is comparable to the energy lost in the evaporation of atoms and is much higher than the kinetic energy of atoms. Therefore, the release of energy as a result of condensation alters the nature of changes in temperature when a gas expands.

This can be demonstrated by considering the first stage of the condensation process when molecules form in an atomic beam. Let us assume that the beam expands in vacuum, i.e. that the gas pressure in the beam is considerably higher than the pressure of the buffer gas which the beam enters, and let us find the nature of the change in temperature in the course of adiabatic expansion of the beam. When the formation of molecules is ignored, the change in the beam tem-perature in the course of its expansion is given by Eqn (2.5).

The change in the internal energy of the system during expansion is

$$dE = dQ + p \, dV \,, \tag{3.16}$$

where p is the gas pressure, V is the volume of the gas element under consideration, and Q is the energy of atoms and molecules contained in this element. Let us assume that there are n_a atoms and n_m molecules in this volume element. Let us assume specifically that $\hbar \omega \ll T \ll D$, where $\hbar \omega$ is the vibrational energy and D is the dissociation energy of the molecule. We then have

$$Q = \frac{3}{2}Tn_{\rm a} + \left(\frac{7}{2}T - D\right)n_{\rm m} \ .$$

Moreover, assuming that the equilibrium between atoms and molecules can be described by the scheme

$$2A \overrightarrow{=} A_2$$
,

we find that the numbers of atoms and molecules are related by the Saha formula:

$$n_{\rm a}^2 n_{\rm m}^{-1} \propto T^{-1/2} \exp(-D/T)$$
,

i.e.

$$2\frac{\mathrm{d}n_{\mathrm{a}}}{n_{\mathrm{a}}} - \frac{\mathrm{d}n_{\mathrm{m}}}{n_{\mathrm{m}}} = \frac{\mathrm{d}T}{T} \left(\frac{D}{T} - \frac{1}{2}\right)$$

Since the total number of the condensation nuclei is conserved in this process, it follows that $2 dn_a + dn_m = 0$, i.e.

$$\frac{\mathrm{d}n_{\mathrm{a}}}{\mathrm{d}T} = \frac{1}{n_{\mathrm{a}}^{-1} + n_{\mathrm{m}}^{-1}} \frac{1}{2T} \left(\frac{D}{T} - \frac{1}{2} \right) \ . \tag{3.17}$$

The total number of atoms and molecules in the gas element under consideration is $n = n_a + n_m$. We have

$$dQ = \left[\left(\frac{3n_a}{2} + \frac{7n_m}{2} \right) + \frac{3T}{2} \frac{\partial n_a}{\partial T} + \left(\frac{7T}{2} - D \right) \frac{\partial n_m}{\partial T} \right] dT$$
$$= \left[\frac{3n_a}{2} + \frac{7n_m}{2} + \frac{1}{n_a^{-1} + n_m^{-1}} \right]$$
$$\times \left(D - \frac{T}{2} \right) \left(D - \frac{11T}{4} \right) \frac{1}{T^2} dT$$

Since n = NV, where N is the number density of atoms and molecules, the second term in Eqn (3.16) is

$$p\,\mathrm{d}V = -nT\,\frac{\mathrm{d}N}{N} \; .$$

Hence, it follows from the condition of adiabaticity of the process, dE = 0, that the relationship between the gas temperature and the number density is

$$N \propto T^{\kappa} \tag{3.18}$$

and since the fraction of molecules in the gas is $s = n_m/n$, the power exponent becomes

$$\kappa = \frac{3}{2} + 2s + s(1-s)\left(D - \frac{T}{2}\right)\left(D - \frac{11}{4}\right)T^{-2} \quad (3.19)$$

If s = 0, we have the law of expansion of an atomic gas characterised by $\kappa = \frac{3}{2}$. However, since $D \gg T$, the deviation from the above law may be considerable even when the number density of molecules is low. By way of illustration let us consider how the temperature of atoms changes in a beam moving from the evaporating surface when the proportion of molecules in the gas s is low. If s = 0, the relevant dependence is given by Eqn (2.5), which can be stated in the form $T/T_0 = R/R_0$, where R is the beam radius, and R_0 and T_0 are its radius and temperature in the region where the beam is formed.

It follows from the condition $jR^2 \sim TNR^2 = \text{const}$ that

$$\frac{\mathrm{d}R}{R} = -\left(\frac{1}{4} + \frac{\kappa}{2}\right) \frac{\mathrm{d}T}{T} = -\left(1 + \frac{s}{2}\frac{D^2}{T^2}\right) \frac{\mathrm{d}T}{T} \; .$$

It is assumed above that $D \ge T$. Since $s \propto \exp(D/T)$, it follows that $dT = T^2 ds/Ds$ and the solution of the above equation is

$$\ln\left(\frac{R}{R_0}\right) = \ln\left(\frac{T_0}{T}\right) + \frac{s}{2}\frac{D}{T} .$$
(3.20)

This solution is valid for any value of $s \ll 1$ and represents an expansion in terms of the small parameter T/D.

Let us consider the thermal regime of expansion of a gas in which clusters grow. Thermodynamic equilibrium between atoms and large clusters is lost and a further parameter associated with the cluster growth rate is needed in the law which describes the change in temperature with gas expansion. In view of our interest in the growth of charged clusters, the problem can be formulated as follows. It is assumed that the cluster evolution is governed by the processes of the attachment of atoms to clusters and the evaporation of atoms from clusters, i.e. by the processes described by Eqn (3.6). Then the number of clusters in the selected element does not vary with time and only its volume increases. Let us assume also that the cluster size is restricted to a narrow interval $\Delta q \ll \overline{q}$, where $\overline{q}(t)$ is the average number of atoms in a cluster and Δq is the width of the distribution function of clusters in terms of the number of atoms that each of them contains. In addition, let us assume that the number of clusters n_{cl} in the selected element of volume is small compared with the number of atoms n_a in this element. In the case under consideration when the condensation occurs at charged clusters, this condition corresponds to a weak ionisation of the gas or vapour. Let us now see how the gas expands under these thermal conditions.

The internal energy of the gas element under consideration is now given by Eqn (3.16). Since the gas pressure is created by atoms, the second term in Eqn (3.16) is, as before,

$$p\,\mathrm{d}V = -n_\mathrm{a}\frac{T\,\mathrm{d}N_\mathrm{a}}{N_\mathrm{a}} + T\,\mathrm{d}n_\mathrm{a} \ ,$$

where N_a is the number density of atoms and $n_a = N_a V$ is the number of atoms in the gas element in question. The first term of Eqn (3.16) is now

$$dQ = d\frac{3Tn_{a}}{2} + d(3T\bar{q}n_{cl}) - d\sum_{q} E_{q}n_{q} . \qquad (3.21)$$

The first term in the above expression represents the kinetic energy of atoms and the second corresponds to the vibrational excitation of a cluster; $n_{\rm cl} = \sum_q n_q$ is the total number of clusters and \overline{q} is the average number of atoms in a cluster. The cluster is regarded as a macroscopic particle and the energy of the vibrational quanta is thus small compared with the thermal energy. Therefore, the Dulong-Petit law applies to the specific heat of the cluster. In the third term of Eqn (3.21) the quantity E_q is the total binding energy of atoms in a cluster consisting of q atoms. This term includes the internal energy of clusters regarded as a system of bound atoms.

The third term in Eqn (3.21) can be represented in the form

$$\mathrm{d}\sum_{q} E_{q} n_{q} = \frac{\mathrm{d}E_{q}}{\mathrm{d}q} n_{\mathrm{cl}} \,\mathrm{d}\bar{q} = \varepsilon_{q} n_{\mathrm{cl}} \,\mathrm{d}\bar{q} \ ,$$

where ε_q is the binding energy of a surface atom in a cluster. When the value of q is large, so that a cluster becomes a macroscopic particle, this binding energy is $\varepsilon_q = \varepsilon_{sub}$, where ε_{sub} is the sublimation energy of a macroscopic system per atom. The conservation of the total number of atoms in the selected volume element,

$$\mathrm{d}n_\mathrm{a} + n_\mathrm{cl}\,\mathrm{d}\bar{q} = 0 \ ,$$

allows us to reduce the third term of Eqn (3.21) to

$$d\sum_{q}E_{q}n_{q}=-\varepsilon_{\rm sub}\,dn_{\rm a}$$
 .

Since $\varepsilon_{sub} \ge T$ and terms of the order of T/ε_{sub} are small compared with unity, the conservation of the total energy dE = 0 yields

$$\frac{3}{2}\left(1+\frac{2\bar{q}n_{\rm cl}}{n_{\rm a}}\right)\frac{\mathrm{d}T}{T}-\frac{\mathrm{d}N_{\rm a}}{N_{\rm a}}-\varepsilon_{\rm sub}\frac{\mathrm{d}n_{\rm a}}{Tn_{\rm a}}=0 \quad . \tag{3.22}$$

This equation gives the relationship between the density and temperature of the expanding gas at a given rate of condensation of atoms in clusters. Since this rate depends on the gas temperature, the problem of determining the nature of the change in temperature with time becomes self-consistent.

The formal solution of Eqn (3.22) is given by Eqn (3.18) where the parameter κ is

$$\kappa = \frac{3}{2} \left(1 + 2\bar{q}c \right) + c \, \frac{\varepsilon_{\text{sub}}}{T} \, \frac{\mathrm{d}\bar{q}}{\mathrm{d}T} \,, \tag{3.23}$$

and $c = n_{\rm cl}/n_{\rm a}$ is the concentration of the condensation nuclei that does not change during the condensation process. In the absence of clusters (c = 0) Eqn (3.23) corresponds to adiabatic expansion of an atomic gas ($\kappa = \frac{3}{2}$).

The presence of clusters in an adiabatically expanding gas alters the nature of the heat balance. This occurs in the expression for the adiabatic expansion parameter (3.2) in two ways: first, some energy is concentrated in the internal degrees of freedom of a cluster; second, the attachment of atoms to a cluster releases an energy equal to the energy of bond formation.

3.3 Processes of evaporation and coagulation of clusters

Charged clusters grow by the attachment of atoms and simultaneously some atoms evaporate from the cluster surface. We shall allow for these processes in the description of the evolution of a charged cluster in a supersaturated vapour based on the liquid drop model.

We shall derive the balance equation for the growth of a large cluster allowing solely for the processes of attachment of atoms to a cluster. We shall assume that a cluster can be regarded as a liquid drop, so that an atom collides effectively with a macroscopic particle of radius *r*. Moreover, we shall postulate that the cluster size is small compared with the mean free path of atoms. Then the cross section for the attachment of an atom to a cluster is equal to $\pi r^2 \xi$, where ξ is the probability that an atom colliding with a cluster surface becomes attached to it. The balance equation for the number of atoms in a cluster $q \ge 1$ has the following form if only the attachment of atoms is taken into account:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \bar{v}N\pi r^2 \xi \quad , \tag{3.24}$$

where $\overline{v} = (8T/\pi m)^{1/2}$ is the average thermal velocity of the atoms, *m* is the mass of an atom, and *N* is the number density of atoms.

Let us now include in Eqn (3.24) the evaporation of atoms with the aid of Eqns (3.1) and (3.3) for the fluxes representing the attachment of atoms to a cluster and the evaporation of atoms from its surface. The result is

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \left(\frac{8\pi T}{m}\right)^{1/2} r^2 \left\{ N - N_{\mathrm{sat}}(T) \exp\left[-\frac{(\varepsilon_q - \varepsilon_{\mathrm{sub}})}{T}\right] \right\}.$$
(3.25)

The probability of attachment of an atom to a cluster on collision with the latter is assumed to be unity ($\xi = 1$). Within the framework of the liquid drop model the cluster radius can be introduced on the basis of Eqn (3.11): $r = (3q/4\pi\rho)^{1/3}$, where ρ is the density of the liquid. If the balance equation (3.25) is averaged over the number of atoms in a cluster on the basis of the distribution function (2.25), Eqn (3.25) becomes

$$\frac{\mathrm{d}\bar{q}}{\mathrm{d}t} = \bar{q}^{2/3} k_0 \left\{ N - N_{\mathrm{sat}}(T) \exp\left[-\frac{(\varepsilon_{\bar{q}} - \varepsilon_{\mathrm{sub}})}{T}\right] \right\} , \quad (3.26)$$

where

$$k_0 = 1.93\xi T^{1/2} m^{1/6} \rho^{-2/3} . aga{3.27}$$

The rate constants for the case of expansion of a laser copper plasma at a temperature T_c are listed in Table 3 and typical evolution times of this plasma under condensation conditions are given in Table 5.

Table 5. Parameters of condensation of a copper plasma.

	Radiation flux/W cm ^{-2}			
	10 ⁷	3×10^6	10 ⁶	
$\tau_{\rm r}/10^{-5}{\rm s}$	1.5	1.1	0.8	
$t_{\rm c}/10^{-7}{\rm s}$	1.0	2.5	4.6	
$\tau_{\rm exp}/10^{-6}{\rm s}$	4.2	4.4	4.5	
x_{c}/mm	0.08	0.13	0.20	
$\kappa/10^{-17} \mathrm{cm}^3$	1.0	4.2	9.4	
$N_{+}/10^{14} \mathrm{cm}^{-3}$	2.0	1.0	0.6	
$N_{\rm n}/10^{13}{\rm cm}^{-3}$	1.4	1.4	1.8	
$10^{-4} \overline{q}$	3.8	3.2	1.6	
r_0/\rm{nm}	4.7	4.5	3.6	
$r_0 T_c e^{-2}$	0.9	0.7	0.5	

In addition to the growth of clusters by condensation and evaporation of atoms, some role in the cluster growth is also played by the coagulation of clusters, i.e. by the merging of two clusters when they collide. The kinetic equation for the distribution function of clusters in terms of the number of atoms in a cluster f(q, t) has the following form if the processes of spontaneous dissociation of clusters into smaller parts (including evaporation of atoms) are ignored:

$$\frac{\partial f(q,t)}{\partial t} = \int_0^q k(q_1, q - q_1) f(q_1, t) f(q - q_1, t) \, \mathrm{d}q_1$$
$$-f(q,t) \int_0^\infty k(q, q_1) f(q_1, t) \, \mathrm{d}q_1 , \qquad (3.28)$$

where $k(q_1, q_2)$ is the rate constant of coagulation in which the numbers of atoms are q_1 and q_2 to form a cluster with $q_1 + q_2$ atoms and the cluster size distribution function is normalised to N_{cl} , which is the total density of clusters:

$$\int_{0}^{\infty} f(q, t) \,\mathrm{d}q = N_{\rm cl} \quad . \tag{3.29}$$

Integration of Eqn (3.28) with respect to q yields dN/dt = 0. Therefore, the adopted form of the kinetic equation corresponds to the conservation of the total

density of clusters in the course of their coagulation. This is true of the evolution of charged clusters which act as the condensation nuclei. Therefore, the kinetic equation (3.28) describes the evolution of charged clusters.

Condition (2.21) allows us to represent the rate constant of coagulation of two clusters in accordance with Eqn (2.28):

$$k = \left(\frac{8\pi}{T\mu}\right)^{1/2} e^2(r_1 + r_2) = k_c F(q_1, q_2) \quad , \tag{3.30}$$

$$k_{\rm c} = \left(\frac{8\pi}{Tm}\right)^{1/2} {\rm e}^2 \left(\frac{3m}{4\pi\rho}\right)^{2/3}$$

$$= 3.11 {\rm e}^2 T^{-1/2} m^{-1/6} {\rm e}^{-1/3} = 0.24k$$
(3.31)

$$F(q_1, q_2) = \left(\frac{q_1 + q_2}{q_1 q_2}\right)^{1/2} \left(q_1^{1/3} + q_2^{1/3}\right) , \qquad (3.32)$$

and the rate constant $k_{\rm rec}$ is given by Eqn (2.31).

Multiplication of Eqn (3.13) by q and integration with respect to dq (which is the number of atoms in a cluster) gives

$$\frac{\mathrm{d}\bar{q}}{\mathrm{d}t} = k_{\rm c} N \left[\int_0^\infty q \,\mathrm{d}q \int_0^q F(q_1, q - q_1) f(q_1, t) f(q - q_1, t) \,\mathrm{d}q_1 - \int_0^\infty q \,\mathrm{d}q \int_0^\infty F(q_1, q) f(q, t) f(q_1, t) \,\mathrm{d}q_1 \right].$$
(3.33)

We shall use the approximate solution of Eqn (3.28) for the case when the coagulation rate constant of Eqn (3.31) is independent of the number of atoms in a cluster, i.e. $F(q_1,q_2) = \text{const.}$ Then $f(q,t) = N_{cl} \exp(-q/\bar{q})/\bar{q}$ is the solution of Eqn (3.28). Substitution of this solution into Eqn (3.33) yields

$$\frac{d\bar{q}}{dt} = 0.9 k_{\rm rec} N_{\rm cl} \bar{q}^{5/6} , \qquad (3.34)$$

where the rate constant $k_{\rm rec}$ is defined by Eqn (2.31). The divergence between the rate constants in Eqns (2.32) and (3.34) is a measure of the error resulting from the use of the approximate solution.

The application of the same procedures to neutral clusters, in which case the coagulation cross section is $\pi(r_1 + r_2)^2$ —where r_1 and r_2 are the radii of the colliding clusters—gives the following balance equation which replaces Eqn (3.34):

$$\frac{d\bar{q}}{dt} = 1.1 \, k_{\rm coag} N_{\rm cl} \bar{q}^{7/6} \,\,, \tag{3.35}$$

where k_{coag} is defined by Eqn (2.35). Again, the difference between the coagulation rate constants in the balance equations (2.33) and (3.35) is a measure of the error resulting from the approximation adopted to obtain this result.

Eqns (3.34) and (3.35) are of no practical importance because the mutual neutralisation of clusters can occur only once. Nevertheless, the above comparison of the rate constants in Eqns (2.32) and (3.34), and also in Eqns (2.33) and (3.35) is useful because it gives an estimate of 10% for the error of the adopted method.

If condition (2.22) is not obeyed, i.e. if the coagulation cross section is given by Eqn (2.33), the balance equation for the average number of atoms in a cluster becomes

$$\frac{d\bar{q}}{dt} = N_{\rm c}\bar{q}^{5/6} (k_{\rm rec} + k_{\rm coag}\bar{q}^{1/3}) \quad . \tag{3.36}$$

Table 5 gives the evolution parameters of the investigated copper plasma obtained by the analysis described above.

The rate constants defined by Eqns (2.35) and (3.27) differ by a numerical factor, so that

$$\frac{k_{\text{coag}}}{k_0} = 7.0$$

This means that these rate constants can be described by the same expression $k \propto v_a r_a^2$, where $v_a \propto (T/m)^{1/2}$ is the thermal velocity of an atom and $r_a \propto (m/\rho)^{1/3}$ is the radius corresponding to one atom in a condensed system. The same dependence of the rate constants k_{coag} and k_0 on the parameters of the problem is a consequence of the fact that only one combination with the dimensions of the rate constant can be formed from the parameters T, m, and ρ . However, the rate constants are of different nature and are derived from the balance equations that describe different processes. In fact, the condensation rate constant k_0 represents the rate of growth of a cluster because of the attachment of atoms to the cluster, which in the absence of evaporation processes is

$$\left(\frac{\mathrm{d}\bar{q}}{\mathrm{d}t}\right)_{\mathrm{con}} \propto v_{\mathrm{a}} r_{q}^{2} N \quad , \tag{3.37}$$

where $v_a \propto (T/m)^{1/2}$ is the thermal velocity of an atom, $r_q \propto q^{1/3}r_a$ is the size of a cluster, and N is the number density of atoms. This equation allows for the increase in the number of atoms by unity in a cluster when one atom becomes attached. The balance equation for cluster growth by coagulation is

$$\left(\frac{\mathrm{d}\bar{q}}{\mathrm{d}t}\right)_{\mathrm{coag}} \propto v_q r_q^2 N_n \bar{q}$$

Here, $v_q \propto v_a/q^{1/2}$ is a typical velocity of a cluster and N_n is the number density of clusters. Allowance is made for the fact that the coagulation of two clusters increases the number of atoms in a cluster by $\sim \overline{q}$. Therefore,

$$\left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)_{\mathrm{con}} \left(\frac{\mathrm{d}q}{\mathrm{d}t}\right)_{\mathrm{coag}}^{-1} \propto N \left(N_{\mathrm{cl}}\bar{q}^{1/2}\right)^{-1}$$

Hence it follows that as long as the majority of atoms are in a free state, the growth of clusters is governed by the attachment of atoms.

3.4 Lifetime of an excited cluster

The nature of cluster growth depends on the process of coagulation of two clusters. This process is accompanied by modification of many bonds and it is therefore effective if the colliding clusters are liquid. An excited cluster formed by coagulation of two clusters may split into parts. Let us now consider the channels of decay of a cluster and its lifetime.

The process under consideration is

$$A_i + A_j \longrightarrow A_q^* \longrightarrow A_k + A_{q-k}, \quad q = i + j \quad (3.38)$$

where A is an atom. The process can be analysed most simply on the basis of its energy parameters [103, 104]. This analysis will be demonstrated on the basis of the liquid drop model of a cluster. In this case the binding energy of atoms in a cluster containing q atoms is

$$E = \varepsilon_{\infty} q - A q^{2/3} , \qquad (3.39)$$



Figure 5. Energy released as a result of coagulation of two clusters $(A_k + A_{q-k} \rightarrow A_q)$ with the short-range potential of the interaction between atoms. The total number of atoms q in a cluster is assumed to be 40 (1), 50 (2), 60 (3), 70 (4), 80 (5). The data are taken from Refs [105, 106].



Figure 6. Energy released as a result of coagulation of two clusters $(A_k + A_{q-k} \rightarrow A_q)$ with the Lennard-Jones potential for the interaction between atoms. The total number of atoms q in a cluster is assumed to be 40 (1), 60 (2), or 80 (3). The data are taken from Refs [107, 108].

where ε_{∞} is the binding energy per atom in a macroscopic system of bound atoms, and the second term on the righthand side of Eqn (3.39) corresponds to the surface energy and is proportional to the surface area of a cluster. If the cluster is spherical, the energy needed for its dissociation by process (3.38) is

$$\Delta E = A \left[(q-k)^{2/3} + k^{2/3} - q^{2/3} \right] .$$
(3.40)

The probability of this decay process decreases as the above energy increases. It follows from Eqn (3.40) that $\Delta E(k)$ becomes larger when k increases, i.e. the most probable channels of decay of an excited cluster correspond to the release of one atom or a small number of atoms.

Eqn (3.40) is valid in the case of large values of q and k, because small values of k are then of the greatest interest. We shall therefore use the results of a realistic model for a cluster consisting of atoms with a short-range interaction, which describes clusters of rare gases. If the atoms in a solid cluster are regarded as hard spheres, the cluster structure is face-centred cubic or hexagonal. Fig. 5 gives the k dependence of the energy

$$\Delta E(q, k) = E(q) - E(k) - E(q - k) , \qquad (3.41)$$

which is needed for the decay process of Eqn (3.38) at absolute zero when the atoms are close packed in a cluster. The energy parameters of these clusters are taken from Refs [105, 106]. In the case of small clusters the icosahedral structure is preferable and the clusters can then be regarded as soft spheres. Fig. 6 gives the dependence (3.41) for clusters with an icosahedral structure when the interaction between the cluster atoms is described by the Lennard-Jones potential. The energy parameters of these clusters are based on the calculations reported in Refs [107, 108]. In Figs 5 and 6, and below, the binding energies are given in terms of the dissociation energy D of a diatomic molecule. Examination of Figs 5 and 6 leads to the conclusion which also follows from Eqn (3.40) that the liberation of one atom from an excited cluster is the preferred decay channel.

The lifetime of a long-lived cluster formed by the coagulation of two clusters will now be calculated. The statistical model of the distribution of the internal degrees of freedom of the cluster will be used. A cluster with q atoms has s = 3q - 6 vibrational degrees of freedom and the transitions between these degrees establish a statistical

equili-brium. For simplicity, the frequencies of all these vibrations are assumed to be the same and equal to ω . The total number of states in a cluster with the excitation energy ΔE is then

$$W_{ps} = \frac{(p+s-1)!}{p!(s-1)!} , \qquad (3.42)$$

where $p = \Delta E/\hbar\omega$ is the total number of vibrational excitations in the system and s is the number of vibrational degrees of freedom.

The distribution of Eqn (3.42) can be derived as follows. Consider *s* vibrations (oscillators) and *p* excitations. The first oscillator is located at the first position and the other oscillators and excitations follow in a random manner. This gives a certain sequence of oscillators and excitations. We assume that the number of excitations for a given oscillator is equal to the number of the corresponding components in such a sequence which follow the oscillator in question and precede the next oscillator. Then the total number of variants of the distribution of excitations between the oscillators is equal to the number of combinations s - 1 of oscillators which can be formed from the total number of randomly distributed members of the sequence p + s - 1, and is described by Eqn (3.42).

The same method can be used to determine the number of variants such that the excitation energy of the system does not exceed a given value $\Delta E - p\hbar\omega$. The distribution is now

$$W'_{ps} = \frac{(p+s)!}{p!\,s!} \tag{3.43}$$

and can be found by adding to the system in question just one oscillator which takes up the excess energy. Hence, we find the probability that the energy of this oscillator exceeds $\Delta \varepsilon = k\hbar \omega$. The number of such variants is

$$W_{ps}^{k} = \frac{(p-k+s-1)!}{(p-k)!(s-1)!}$$
,

and the probability of this situation is

$$w_k = \frac{W_{ps}^k}{W_{ps}} = \frac{(p+s-k-1)!}{(p+s-1)!} \frac{p!}{(p-k)!} .$$
(3.44)

In particular, if $k \ll p$, this gives

$$w_k = \left[1 + \frac{s-1}{1 + (s-1)(p - \frac{1}{2}k - \frac{1}{2})^{-1}}\right]^{-k} .$$
(3.45)

These expressions can be used to find the lifetime of an excited plasma when the decay involves the release of one atom. This release is assumed to occur when the excitation energy of the relevant oscillator, corresponding to the vibration of an atom in a direction perpendicular to the cluster surface, exceeds the binding energy of a surface atom in a cluster.[†] The average time of a change in this distribution of excitations between oscillators is t_0 . The statistical model then gives the average time after which the number of quanta for a given oscillator exceeds k:

$$\tau_k = t_0 \left[1 + (s-1) \left(p + \frac{k}{2} - \frac{1}{2} \right)^{-1} \right]^k .$$
(3.46)

[†]This corresponds to the Einstein model (see, for example, R ef. [109]) in which each atom is regarded as a three-dimensional oscillator with vibrations independent of the vibrations of other atoms.

If a cluster includes n_{surf} surface atoms with the same binding energy, the lifetime of an excited cluster before the release of one atom is

$$\tau_k = \frac{t_0}{n_{\text{surf}}} \left[1 + (s-1)\left(p + \frac{k}{2} - \frac{1}{2}\right)^{-1} \right]^k .$$
(3.47)

The nature of the process of coagulation of two clusters will now be considered. The average kinetic energy of the relative motion of the two clusters is

$$\bar{E}_{\rm kin} = \frac{\overline{\mu v^2}}{2} = \frac{3T}{2} ,$$

where μ is the reduced mass of the clusters, ν is the velocity of relative motion, and T is the temperature expressed in energy units. The binding energy of the clusters which coagulate considerably exceeds their thermal energy. Therefore, each contact between clusters results in their coagulation and the formation of a long-lived complex. The average energy of each oscillator of this complex is T if $T \ge \hbar\omega$. Therefore, the excitation energy of such a longlived complex is given by the following expression valid for $q \ge 1$ and accurate to within values of the order of T:

$$\varepsilon = 3qT + \Delta E \quad , \tag{3.48}$$

where q is the number of atoms in a cluster and ΔE is the energy released as a result of cluster coagulation. The values of this quantity for the short-range and Lennard-Jones potentials of the interaction of atoms in a cluster are given in Figs 5 and 6.

It therefore follows from Eqns (3.47) and (3.48) that the lifetime of an excited cluster before the release of one atom is $(p = \varepsilon/\hbar\omega, s = 3q, q \ge 1)$:

$$\tau = \frac{t_0}{n_{\text{surf}}} \left[1 + \frac{\hbar\omega}{T + (\Delta\varepsilon/\hbar\omega)} \right]^{\Delta\varepsilon/\hbar\omega} , \qquad (3.49)$$

where $\Delta \varepsilon$ is the binding energy of the released atoms. If it is assumed — as in Eqn (3.48) — that $T \ge \hbar \omega$, the result $(\Delta \varepsilon > T)$ is

$$\tau = \frac{t_0}{n_{\text{surf}}} \exp\left[\Delta\varepsilon \left(T + \frac{\Delta E}{3q}\right)^{-1}\right]$$
(3.50)

For large clusters such that $q \gg \Delta E/(3\Delta \varepsilon) \propto q^{2/3}$, the above expression gives

$$\tau = \frac{t_0}{n_{\text{surf}}} \exp \frac{\Delta \varepsilon}{T} \ . \tag{3.51}$$

We can see that these expressions do not include the dependence on the parameter $\hbar\omega$, which represents the energy of a quantum of vibrational excitations. The lifetime of a long-lived complex may be expected to depend weakly on the frequency distribution of the vibrations in a cluster. Moreover, the temperature dependence of t_0 is a power law and it is weak compared with the exponential dependence of Eqn (3.51) for the lifetime of a complex, which is governed by the exponential factor $\exp(\Delta\varepsilon/T)$.

This dependence can be obtained more simply on the assumption that the release of an atom occurs when the energy of the relevant vibration exceeds the binding energy $\Delta \varepsilon$ of an atom. It follows from the Boltzmann law that the probability of this happening is proportional to $\exp(-\Delta \varepsilon/T_{\rm eff})$, where $T_{\rm eff}$ is the effective temperature of a cluster and is equal to the ratio of the excitation energy of the cluster to the number of vibrations, i.e.

 $T_{\rm eff} = (3qT + \Delta E)/3q$. This gives the temperature dependence in Eqns (3.50) and (3.45).

In the $q \ge 1$ case under consideration it follows from Eqn (3.40) that $\Delta E \propto q^{2/3}$ ($k \propto q$) and this gives $\Delta E/3q \propto q^{-1/3}$, i.e. $(T_{\text{eff}} - T) \propto q^{-1/3}$. The temperature of a long-lived complex formed by the coagulation of two clusters is therefore close to the temperature of the colliding clusters if $q \ge 1$.

The lifetime of a long-lived complex is determined by its decay accompanied by the release of one atom, because the release of molecules requires a higher energy and the dependence of the lifetime on the energy lost is strong. Consequently, the relationship between the lifetimes for different decay channels is

$$\tau_1 < \tau_2 < \tau_3 < \dots$$
, (3.52)

where τ_i is the lifetime of a complex until the release of a molecule with *i* atoms. This equality breaks down at high values of $i \sim q$, but these values of *i* do not contribute to the lifetime of a long-lived complex.

The lifetime of such a complex before the release of a diatomic molecule follows from Eqn (3.52):

$$\tau_2 = \frac{t_0}{n_2} \exp\left[\Delta\varepsilon_2 \left(T + \frac{\Delta E}{3q}\right)^{-1}\right] , \qquad (3.53)$$

where n_2 is the number of ways in which a diatomic molecule with the surface binding energy $\Delta \varepsilon_2$ can be released from a cluster. The minimum binding energy of a molecule for the short-range interaction of atoms in a cluster is

$$\Delta \varepsilon_2 = 2\Delta \varepsilon - D \quad , \tag{3.54}$$

where $\Delta \varepsilon$ is the binding energy of an atom in a cluster and D is the dissociation energy of a diatomic molecule. If each surface atom has p nearest neighbours with the same energy, the number of ways that a diatomic molecule can be released is

$$n_2 = C_{n_{\text{surf}}}^p = \frac{n_{\text{surf}}!}{p! (n_{\text{surf}} - p)!} , \qquad (3.55)$$

where n_{surf} is the number of surface atoms with the minimum binding energy. For close-packed clusters the number of nearest neighbours which belong to the same shell is p = 0.1, or 2. If p = 0, the minimum binding energy of a diatomic molecule exceeds the value given by Eqn (3.54) and the lifetime of a long-lived complex to the moment of release of a diatomic molecule becomes even greater.

Table 6 lists the ratios of the lifetimes of a long-lived complex before the release of an atom and of a diatomic molecule when the interaction of atoms in a cluster is of the short-range type. It is assumed that the configuration of atoms in a close-packed cluster at a given temperature is the same as at absolute zero. This is true of solid clusters. The melting of close-packed clusters occurs at T = 0.3D, where D is the dissociation energy of a diatomic molecule [110, 111]. Melting transfers some of the surface atoms to vacant excited shells. This considerably reduces the lifetime of a cluster before the release of an atom but the lifetime before the release of a diatomic molecule is not affected as much because of the random positions of the excited atoms. It follows that the decay by the release of a single atom is even more important in the case of liquid clusters than for the solid ones.

Table 6. Ratio τ_1/τ_2 of the lifetimes of an excited cluster with the short-range interaction of atoms in the case of the release of an atom (τ_1) and of a diatomic molecule (τ_2) [116].

Cluster	T = 0.1D	T = 0.2D	T = 0.3D
A ₅₅	8×10^{-22}	6×10^{-7}	2×10^{-7}
A ₅₆	1×10^{-14}	4×10^{-8}	7×10^{-6}
A ₅₇	1×10^{-18}	7×10^{-10}	8×10^{-7}
A ₅₈	1×10^{-21}	9×10^{-11}	4×10^{-7}
A ₅₉	1×10^{-21}	8×10^{-11}	4×10^{-7}
A ₆₀	3×10^{-14}	1×10^{-7}	2×10^{-5}

A long-lived complex formed by the coagulation of two colliding clusters thus decays primarily by the release of one atom. Therefore, the collision of two clusters producing a long-lived complex occurs in accordance with the scheme [116]

$$A_i + A_j \longrightarrow A_q^* \longrightarrow A_{q-1} + A \longrightarrow A_{q-2} + 2A \dots , \qquad (3.56)$$

and the lifetime of this complex increases after each consecutive decay. Table 7 [116] gives the lifetimes of intermediate complexes which begin with the formation of a cluster A_{60} at the indicated temperatures. The reduction in the temperature of a cluster as a result of each consecutive decay is taken into account.

Table 7. Lifetimes of long-lived complexes formed by the successive decay of clusters beginning from A_{60} at the given temperature. The lifetimes are in units of t_0 , which is a typical time in which a given distribution of excitations at the appropriate oscillators is lost [116].

	T = 0.2D	T = 0.3D	T = 0.4D
τ_{60}	2×10^{10}	6×10^{6}	$9 \times 10^{5 a}$
$ au_{59}$	6×10^{11}	1×10^{7}	9×10^{4} a
$ au_{58}$	2×10^{14}	1×10^{8}	3×10^{5} a
τ_{57}	2×10^{18}	2×10^{9}	1×10^{6}
τ_{56}	_	9×10^{10}	6×10^{6}
τ_{55}	—	1×10^{13}	3×10^7

^a This lifetime corresponds to a solid cluster, but it is actually liquid at this temperature and has a shorter lifetime.

The results given above and general considerations make it possible to describe the nature of the decay of a long-lived complex formed as a result of coagulation of two clusters. The decay involves the consecutive release of several atoms and after the release of each atom the temperature of a cluster falls and its lifetime increases. After the liberation of a small number of atoms the lifetime increases by several orders of magnitude and the cluster becomes effectively stable. For example, the excitation energy of a cluster A_{60} at a temperature T = 0.2D is sufficient for the release of seven atoms, but after the liberation of three or four atoms the lifetime becomes practically infinite.

The expressions obtained for the lifetime of an excited cluster include a strong temperature dependence, because a complex is formed at $T \ll D$. Therefore, in the lifetime estimates we have to use the real binding energies of the atoms that are released and approximate models, such as the model of a liquid drop for a cluster, are unacceptable.



Figure 7. Lifetime of a liquid cluster A_{13} with the Lennard-Jones potential for the interaction of atoms: (1) Eqn (3.55); results of computer simulation of the cluster behaviour taken from Ref. [114] (2), Ref. [115] (3), and Ref. [116] (4).

The expressions obtained apply to a solid cluster because the harmonic nature of vibrations is implied. The lifetimes of liquid Lennard-Jones clusters have been calculated by computer simulation of the motion of atoms in clusters [112–114]. Although the error resulting from the application of Eqn (3.50) to a liquid cluster is large, we shall nevertheless use this equation in a comparison with computer calculations for liquid Lennard-Jones clusters A_{13} . It is necessary to bear in mind that the liquid state of a Lennard-Jones cluster A_{13} , which has an icosahedral structure, corresponds to the transfer of one atom to a vacant layer and the energy of such a transfer is $\varepsilon_0 = 2.86D$ [108, 115]. The decay of a cluster is governed by the release of this atom with the binding energy $\Delta \varepsilon = 3.56D$ [108]. Eqn (3.50) then becomes

$$\tau = t_0 \exp\left[\frac{(3q-7)\Delta\varepsilon}{E_{\rm ex} - \varepsilon_0}\right] , \qquad (3.57)$$

where $E_{\rm ex}$ is the excitation energy of a cluster; a redistribution of the energy between 3q-6 vibrations (q=13) is taken into account. Use is made of the expression $t_0 = R_{\rm e}(2D/m)^{-1/2}$ for a typical time of a change in the distribution, where *m* is the mass of an atom, and $R_{\rm e}$ and *D* are the parameters of a diatomic molecule.

Fig. 7 gives the lifetime of the Lennard-Jones cluster A_{13} obtained by computer simulation of the cluster and by the application of Eqn (3.57). The error resulting from the use of this expression increases with increasing cluster excitation energy. The discrepancy between this expression and the results of computer simulation increases severalfold if the nonlinear effects are taken into account. Nevertheless, this equation is suitable for estimating the order of magnitude of the lifetime of a liquid cluster. Its simplicity makes it convenient for this purpose.

We shall use the results obtained to analyse the growth of clusters during expansion and cooling of a vapour. Various mechanisms of cluster growth are possible, depending on the nature of the interaction of atoms and clusters. We shall consider the limiting cases. If the surface of a cluster is regarded as solid, then the growth is governed solely by the attachment of atoms to the cluster and by the evaporation of atoms in accordance with the scheme given by Eqn (3.6):

$$A_q + A \overrightarrow{A}_{q+1}$$
.

If it is assumed that the surface of a cluster is soft or liquid, the growth resembles coalescence of liquid drops which occurs in accordance with the scheme

$$A_i + A_j \overrightarrow{\longrightarrow} A_q, \quad i + j = q \quad . \tag{3.58}$$

This analysis implies an intermediate scheme

$$A_i + A_j \longrightarrow A_q^* \longrightarrow A_{q-p} + pA \quad . \tag{3.59}$$

We shall estimate the number of atoms p released by this process in the case when $i, j \ge 1$. If the decay of a cluster terminates when its temperature reaches the initial temperature of the colliding clusters, then

$$\Delta E = p \Delta \varepsilon \quad , \tag{3.60}$$

where ΔE is the energy released as a result of the coagulation of clusters and $\Delta \varepsilon$ is the binding energy of an atom in the resultant cluster. The maximum energy ΔE for a given value of q corresponds to i = j = q/2. Estimates can now be obtained for clusters with the short-range interaction of atoms. In this case the surface energy of a cluster is $7.8Dq^{2/3}$ [105, 106], where D is the dissociation energy of a diatomic molecule and q is the number of atoms in a cluster. For a large cluster, as in the case of a macroscopic system, we have $\Delta \varepsilon = 6D$ since each atom has 12 nearest neighbours. This gives

$$p \le \Delta E_{\max} (\Delta \varepsilon)^{-1} = 0.34 q^{2/3}$$
 (3.61)

In particular, $p \leq 4$ if q = 41 and $p \leq 5$ if q = 57. We can therefore assume that $p \leq q$ and this makes it possible to neglect p compared with q, which corresponds to the growth of clusters by coagulation described by the scheme in Eqn (3.58). This scheme also describes the growth of clusters with a liquid surface.

4. Radiation from a hot gas containing clusters

4.1 Radiation from small macroscopic drops

The heat balance may be affected not only by the processes of gas expansion and condensation, but also by the radiation emitted from clusters. The formation of clusters does indeed alter the radiative properties of the system because large clusters, behaving as macroscopic particles, absorb in a wide spectral range. Therefore, the emission of radiation by an expanding gas or a plasma is greatly enhanced by the formation of clusters. It is therefore desirable to estimate the contribution made by the emission of radiation of an expanding gas to its heat balance.

The radiation from an expanding gas, including a weakly ionised gas, is emitted mainly by the clusters which the gas contains. In fact, the temperature of such a gas, considered on the electron energy scale, is low and therefore the density of excited atoms in the gas is low. Consequently, the power emitted as a result of radiative transitions involving excited atoms is very low and it is at least several orders of magnitude less than the power of the radiation emitted by a gas discharge. Therefore, in contrast to a gas discharge, the excitation of atoms in a plasma of this kind makes no contribution to the emission of radiation. The radiation generated in such a plasma originates from large clusters present in it, in the same way as the radiation from hydrocarbon flames is determined by the soot particles present in them [117].

Let us consider how the nature of the radiation emitted by a cluster changes with its growth. The absorption and emission spectra of atoms consist of separate lines. In the case of molecules these lines are transformed into bands and each of them consists of a large number of lines. As the number of atoms in a cluster molecule increases, the bands and lines expand and intersect. If the number of atoms in a cluster is large, the absorption spectrum extends over a certain range of wavelengths where the absorption probability (or the power of the radiation emitted by a cluster) depends smoothly on the wavelength. This means that the macroscopic limit is reached and we shall therefore assume that the absorption spectrum does not change as a result of further growth of a cluster. This simplified analysis of the nature of the emission from a cluster does not provide a rigorous analysis of the emission spectrum of a gas containing clusters, but it is convenient for estimating the contribution of radiation to the heat balance of the system.

In this analysis of the radiative parameters of the investigated plasma, the plasma will be regard as a heated gas containing clusters. For simplicity, these particles will be considered to be spherical. Moreover, in the investigated part of the spectrum (optical and infrared) and for the size of particles in question, the following condition is obeyed by the emission wavelength λ :

$$\lambda \gg r_0 \quad , \tag{4.1}$$

where r_0 is the characteristic particle size.

The photon-absorption cross section of a small spherical particle of radius r, considered in the macroscopic limit, is [118]

$$\sigma_{\rm abs}(\omega) = \frac{12\pi\omega r^3 \varepsilon''}{c[(\varepsilon'+2)^2 + \varepsilon''^2]} , \qquad (4.2)$$

where ω is the electromagnetic wave frequency, c is the velocity of light, and ε' and ε'' are the real and imaginary parts of the permittivity of the particle material. We can now go over to the spectral power of the radiation which, in accordance with the Kirchhoff law, relates the rates of the radiation emission and absorption processes [118]

$$I(\omega) = 4\pi c \sigma_{\rm abs}(\omega) i(\omega) \quad , \tag{4.3}$$

where $i(\omega)$ is the spectral density of blackbody radiation per unit volume and for unit solid angle:

$$i(\omega) = \hbar \omega^3 \left\{ 4\pi^3 c^3 \left[\exp\left(\frac{\hbar \omega}{T}\right) - 1 \right] \right\}^{-1} .$$
 (4.4)

If the frequency dependence of the permittivity is weak, we can find the total radiation power emitted by a small particle:

$$P(\omega) = \int I(\omega) \,\mathrm{d}\omega = 4\pi r^3 f(\omega) k \,\sigma T^5 (\hbar c)^{-1} \,. \tag{4.5}$$

Here, σ is the Stefan-Boltzmann constant, $f(\omega) = 12\epsilon'' [(\epsilon'+2)^2 + \epsilon''^2]^{-1}$, and the parameter k is given by $\int_{0}^{\infty} x^4 = [\int_{0}^{3} x^{-1} dx^{-1}]^{-1}$

$$k = \int_0^\infty \frac{x^4}{\exp x - 1} \, \mathrm{d}x \left[\int_0 (\exp x - 1)^{-1} \, \mathrm{d}x \right]^{-1} = 3.83 \; .$$

The method selected for the representation of the radiation power emitted by a particle makes it possible to compare Eqn (3.38) with the expression for the radiation power emitted by an absolutely black particle $P_0 = 4\pi r^2 \sigma T^4$. We can see that

$$\frac{P_{\rm rad}}{P_0} = kfrT \left(\hbar c\right)^{-1} = 4.9f \frac{r}{\lambda_{\rm m}} , \qquad (4.6)$$

i.e. this ratio is proportional to the small parameter r/λ_m of Eqn (4.1) and the wavelength $\lambda_m = 0.29 \text{ cm} (\text{K}/T)$ corresponds (in accordance with Wien's law) to the maximal spectral radiation power for an ideal blackbody. The photon energy corresponding to the maximum of the spectral power of the radiation emitted by a small particle is somewhat greater (by a factor of 1.2) than the maximum photon energy in blackbody radiation at a given temperature.

Let us now consider this result in relation to the radiation emitted by a hot gas containing small particles. It is important to stress that the power of the emitted radiation is proportional to the volume of a particle. This means that the radiation power obtained from a unit volume is proportional to the mass of the particles per unit volume and is independent of the particle size distribution. Therefore, the radiation power from a unit volume can be found simply by considering the mass of the matter which is present in this volume in the form of large clusters.

In estimating the radiation power emitted by a plasma we shall employ the spectral parameters of soot [119]. In this case† we have $f = 0.9 \pm 0.1$ [120, 121] and the error of 0.1 represents the change in this parameter in the optical frequency range. The radiation power per unit volume of the emitting particles is therefore

$$\frac{P_{\rm rad}}{V} = \gamma T^5 \quad , \tag{4.7}$$

† If it is assumed formally that $\varepsilon', \varepsilon'' > 0$, the maximum value of the parameter $f(\omega)$ is f = 3 and corresponds to $\varepsilon' = 0$, $\varepsilon'' = 2$.

where V is the volume of the emitting material which is in the cluster state, and the parameter of γ for soot is [122, 123]

$$y = 2.5 \pm 0.2 \text{ W cm}^{-3} \text{ K}^{-5}$$
 (4.8)

We shall use the above ratio in estimates. We shall consider the contribution made to the cluster energy balance by the emisison of radiation. We shall do this by writing down the energy balance equation per unit volume of a plasma, associated with the loss of radiation:

$$C_p \frac{\mathrm{d}T}{\mathrm{d}t} = -P_{\mathrm{rad}} = -C_p T \tau_{\mathrm{r}}^{-1} \ . \tag{4.9}$$

The values of τ_r found in this way for our copper plasma example are given in Table 5. They are calculated from Eqn (3.42), which gives $\tau_r = C_p/4\gamma T^4$, on the assumption that all the copper vapour is transformed into large clusters and that the process of emission of radiation occurs at temperatures close to T_c . Moreover, the radiative parameter [Eqn (4.8)] of soot is used for copper. The values of τ_r considerably exceed characteristic plasma expansion times.

This means that the emission of radiation makes only a small contribution to the heat balance of an expanding plasma.

Our analysis of the radiative parameters of a cluster is based on the simplest model of the interaction of radiation with the cluster, which is regarded as a macroscopic particle with the simplest absorption spectrum. In reality, this interaction is more complex and fuller information is needed on the emission spectrum of a particle, which depends on its dimensions (see, for example, Refs [124-126]). When radiation is emitted by metallic clusters (and this review is concerned mainly with such clusters), the absorption spectrum exhibits a strong resonance at the electron plasma frequency of the metal. The width of this resonance is of the order of $v_{\rm F}/r_0$, where $v_{\rm F}$ is the Fermi velocity of the metal electrons and r_0 is the radius of a cluster regarded as a macroscopic particle (see, for example, Ref. [127]). All this means that the expressions obtained for the radiative parameters of clusters can be used only in estimates. In particular, in the specific case of an expanding laser copper plasma this simple approach convincingly demonstrates that the radiation makes no contribution to the heat balance of an expanding beam.

4.2 Photoabsorption cross section of metallic clusters

This rough model of the emission of radiation by a gas con-taining small particles is helpful and has become the first step in an analysis of the process. In the case of condensation of an expanding gas or of a gas escaping from a nozzle this model leads to the conclusion that the radiation emitted by such a system makes no contribution to the energy balance of the system. Another important conclusion of this analysis for a transparent system is that the power of the radiation generated by clusters is proportional to the total mass of the light-emitting particles, i.e. it is proportional to the number of atoms contained in the clusters. Consequently, the absorption cross section of a cluster is proportional to the number of atoms in it and, within the framework of the model adopted earlier on the assumption that f = const, the absorption cross section of a soot particle is

$$\sigma_{\rm abs} = \frac{\sigma_0 a\omega}{\omega_0} \ , \tag{4.10}$$

where *a* is the number of carbon atoms in a particle. If we select $\hbar\omega_0 = 3 \text{ eV}$, we find that the absorption cross section per atom in Eqn (4.10) is

$$\sigma_0 = \frac{m_0 f \omega_0}{4 c \rho} = 7.7 \times 10^{-19} \text{ cm}^2 ,$$

where m_0 is the mass of a carbon atom and ρ is the density of soot particles, assumed to be the same as for graphite.

One further conclusion applied to the radiation emitted by small particles: the emission spectrum of such particles may differ from the emission spectrum of large systems composed of the same material. This is demonstrated in Fig. 8 [124], which gives the absorption cross section of niobium clusters divided by the number of atoms in a cluster, alongside the absorption spectrum of the macroscopic system.



Figure 8. Photoabsorption cross section per atom, calculated for niobium clusters from Eqn (4.2) (continuous curve) and the absorption spectrum of macroscopic niobium (dotted line) [125].



Figure 9. Apparatus used in determining the photoabsorption cross section of silver clusters [128]. The clusters are generated by bombardment of a silver target (1) with 25 keV xenon ions generated in a source (2). The resultant beam of cluster ions is focused and accelerated by ion optics (3) and selected in accordance with their masses by passage through a Wien filter (4). In the interaction region (5) the charged cluster beam moves opposite to a laser beam (6). Charged clusters are excited in

this region and the beam then passes through a static quadrupole deflector (7) which works on the principle of energy selection in an electric field. Therefore, photo-dissociated clusters cannot reach a detector (8). A pulsed laser is used and the deflection of the cluster beam under the influence of laser radiation is a measure of the photoabsorption cross section of the cluster ions.

Methods for the determination of the absorption cross sections of clusters have been developed recently. These methods are being applied to metallic clusters, so that we shall begin with an analysis of the nature of the cross section of a metallic cluster. We shall begin with Eqn (4.2) and macroscopic values of the permittivity of a metal. Bearing in mind that the absorption is due to electrons and that the metal electrons can be regarded as quasiparticles, we find that the permittivity of the metal plasma is

$$\varepsilon = 1 - \frac{\omega_{\rm p}^2}{(\omega^2 + i\omega/\tau)} \ . \tag{4.11}$$

Here, $\omega_p^2 = 4\pi N_e e^2/m_*$ is the plasma frequency of the metal electrons, N_e is the number density of electrons, m_* is the effective mass of electrons in a metal, and τ is the damping time of plasma oscillations, such that $\omega \tau \ge 1$.

Corrections allowing for the difference between a cluster and a macroscopic system are needed in Eqn (4.11). The first of these corrections should allow for the dependence of the decay time of a plasmon on the cluster size. This time is usually represented in the form

$$\frac{1}{\tau} = \frac{1}{\tau_{\infty}} + \frac{v_{\rm F}}{L} ,$$

where τ_{∞} is the time constant of a particle of infinite size, $v_{\rm F}$ is the Fermi velocity, and *L* is the effective scattering length, which in this case is governed by the cluster size. Moreover, the finite cluster size should also be reflected in other parameters of the interaction of electrons with an electromagnetic wave. The general nature of the frequency dependence is conserved and leads to a resonant type of radiation, with the resonance corresponding to $\varepsilon' + 2 = 0$ in Eqn (4.2), i.e. it occurs at the frequency $\omega_0 = \omega_p \sqrt{3}$. Therefore, the cross section representing the absorption of an electromagnetic wave by a metallic cluster can be represented as follows:

$$\sigma_{\rm abs}(\omega) = \frac{\sigma_0 \Gamma^2}{\left(\hbar\omega - \hbar\omega_0\right)^2 + \Gamma^2} \ . \tag{4.12}$$

The width Γ of the resonance and the resonance frequency ω_0 depend slightly on the number of atoms in a cluster, and the maximum absorption cross section σ_0 of a cluster is quite accurately proportional to the number of atoms in a cluster.



Figure 10. Apparatus used in determination of the photoexcitation cross sections of large cluster ions [129]: (1) source of clusters where metallic vapour is mixed with a helium stream kept at liquid nitrogen temperature; (2) laser beam for cluster photoionisation; (3) system for acceleration and focusing a beam of charged clusters; (4) filter for selection of ions in accordance with their masses; (5) laser beam for excitation of cluster ions; (6) region of interaction of charged cluster and laser beam; (7) ion acceleration and deceleration system; (8) time-of-flight mass spectrometer.

In particular, if we use Eqn (4.1) for the photoabsorption cross section and Eqn (4.11) for the permittivity of a metal, we obtain the following expression for the parameters that occur in Eqn (4.12):

$$\Gamma = \frac{\omega_0^2}{\omega \tau (\omega + \omega_0)}, \quad \sigma_0 = \frac{4\pi \omega^4 r^3 \tau}{c\omega_0^2}.$$
(4.13)

These expressions demonstrate that the radiation emitted by metallic and dielectric (insulating) clusters is of the same origin and that the photoabsorption cross section is related to the permittivity parameters of the cluster material.

The experimental methods for determining the photoabsorption cross section of clusters utilise the circumstance that an excited cluster subsequently decays, i.e. that the excitation is lost in the breaking of bonds in a cluster. Therefore, the photoabsorption cross section may be found from a comparison of the mass spectrum of a cluster beam before and after illumination. Figs 9 and 10 show schematically the apparatus used in these experiments. We can see that the principal difference between the apparatus shown in these two figures is that in the case of the photoabsorption by small clusters the interaction time of the radiation with a cluster is increased by directing the incident laser beam parallel to the cluster beam, whereas in the case of larger clusters with a relatively large photoabsorption cross



Figure 11. Changes in the mass spectra of charged potassium clusters obtained for different laser radiation powers [130]; q is the number of atoms in the detected ions. Initially the distribution of the cluster ion masses has the Poisson profile with its centre corresponding to K_{900}^+ ions. The arrows identify the numbers of atoms in cluster ions corresponding to the maximum of the distribution function.

section the laser beam used to excite clusters is directed perpendicular to the cluster beam. Moreover, in the case of large clusters it is convenient to employ multistage excitation. An analysis of the mass spectra of clusters recorded after excitation is based on the assumption that the photoexcitation cross section of a cluster is a monotonic function of the number of atoms in the cluster. The change in the mass spectrum of the cluster ions can then give information on the photoexcitation cross section. By way of demonstration, Fig. 11 [130] shows how the mass spectrum of potassium cluster ions changes with the power of laser radiation if during the ini-tial stage the distribution of the mass of clusters is concentrated near ions with 900 atoms. We can see that an increase in the laser radiation power shifts the distribution function of the resultant cluster ions in the direction of smaller masses.

Let us now consider the results of determination of the absorption cross sections of clusters, which are given in Figs 12-14 for small metallic clusters and in Figs 15-17 for large clusters. We shall not go into the details of the theory (which is given, for example, in Refs [124–126, 135]), but we shall discuss the nature of the excitation of metallic clusters from practical positions. We can see that in the majority of cases the excitation of clusters can be described in terms of the excitation of a plasmon, so that the excitation cross section is given by Eqn (4.12).



Figure 12. Photoabsorption cross sections of silver cluster ions [128]: (a) Ag_9^+ ; (b) Ag_{21}^+ .

The parameters in this equation are listed for some clusters in Table 8. The maximum photoabsorption cross section of clusters of this type is proportional, within the limits of the experimental error, to the number of atoms in a cluster. Moreover, this cross section decreases when the energy of a resonance or its width are increased. It follows from Table 8 that the parameter $\sigma_0 \Gamma \hbar \omega_0$ depends weakly on the nature of the cluster. A statistical analysis of Table 8 yields the average value of this param-eter:

$$\sigma_0 \Gamma \hbar \omega_0 = (1.9 \pm 0.5) \times 10^{-16} \,\mathrm{cm}^2 \,\mathrm{eV}^2 \ . \tag{4.14}$$

It also follows from Table 8 that the photoabsorption cross section is proportional (within 25%) to the number of

Table 8. Parameters of a plasma resonance for metallic cluster ions.

Ion	R ef.	$\hbar\omega_0/{ m eV}$	Г/eV	$\frac{\sigma_0}{10^{-16}\mathrm{cm}^2}$	$\frac{\sigma_0/q}{10^{-16}\mathrm{cm}^2}$	$\frac{\sigma_0 \varepsilon \Gamma/q}{10^{-16} \mathrm{cm}^2 \mathrm{eV}^2}$
$\frac{1}{Ag_{0}^{+}}$	[128]	4.02	0.62	8.84	1.0	2.4
Ag_{21}^+	[128]	3.82	0.56	16.8	0.8	1.7
K_{9}^{+}	[132]	1.93	0.22	26	2.9	1.2
K_{21}^{+}	[132]	1.98	0.16	88	4.2	1.3
K_{500}^{+}	[130]	2.03	0.28	1750	3.5	2.0
K_{900}^{+}	[130]	2.05	0.4	2500	2.8	2.3
Li ⁺ ₁₃₉	[133]	2.92	0.9	62	0.45	1.2
Li_{270}^{+}	[133]	3.06	1.15	120	0.44	1.6
Li_{440}^{+}	[133]	3.17	1.32	280	0.64	2.7
Li_{820}^{+}	[133]	3.21	1.10	440	0.54	1.9
Li ⁺ ₁₅₀₀	[133]	3.25	1.15	830	0.55	2.1



Figure 13. Photoabsorption cross sections of sodium cluster ions [131]; (a) Na_{9}^{+} ; (b) Na_{11}^{+} ; (c) Na_{21}^{+} .

atoms in a cluster. This is of the same order as the error in determining the absolute values of the cross section.

In some cases (Figs 13 and 16) the photoabsorption cross section of clusters, considered as a function of the photon energy, has a doublet structure [131, 134, 135]. The simplest model that can account for this process [131, 135] introduces not only a plasma resonance at a frequency ω_0 , but also a one-electron resonance at a frequency ω_e . Then, the permittivity of a cluster can be described by

$$\varepsilon = 1 - \frac{\omega_0^2}{\omega^2 + i\omega\Gamma} - \frac{F\omega_e^2}{\omega_e^2 - \omega^2 - i\omega\gamma} , \qquad (4.15)$$

where the widths of the plasma Γ and of the one-electron F resonances are in frequency units. In particular, for a Na⁺₂₁ cluster the parameters in the expression describing the measured cross section are

$$\hbar\omega_0 = 2.62 \text{ eV}, \quad \hbar\omega_e = 2.65 \text{ eV}, \quad \Gamma = 0.17 \text{ eV},$$

 $\gamma = 0.01 \text{ eV}, \quad F = 6 \times 10^{-4}$.



Figure 14. Photoabsorption cross sections of potassium cluster ions [132]: (a) K_9^+ ; (b) K_{21}^+ .

We can see that the correction due to intrinsic oscillations of the valence electrons occurs in the above expression, but its relative weight is small.

4.3 Cluster ions in light sources

The above information on the radiative properties of metallic clusters makes it possible to analyse the feasibility of using clusters or cluster ions as the radiative components in light sources. As long as the cluster size is considerably less than the radiation wavelength, the radiation emitted by a cluster is generated by all its atoms. In this respect, a cluster is a more effective light source than an incandescent element where the radiation is generated on the surface. Another advantage of a cluster as a radiative component is its ability to operate at higher temperatures, particularly if clusters can evaporate, i.e. if they are under nonequilibrium conditions. These advantages of clusters make them promising light sources. Therefore, prototypes of cluster lamps are currently being developed: for example, light sources with clusters in the form of compounds of tungsten and thorium have been described in the literature [136].

We shall now consider the general problems of nonequilibrium light sources when the light-emitting particles are clusters. It should be stressed that the condition for the operation of such sources is that the lifetime of a cluster should be considerably longer than the time during which

[†] It is more correct to compare the radiation wavelength with the depth of penetration of the electromagnetic radiation into a metal.



Figure 15. Photoabsorption cross sections of lithium cluster ions [133]: (a) Li^+_{139} ; (b) Li^+_{270} ; (c) Li^+_{820} ; (d) Li^+_{1500} .

the cluster emits energy comparable to the binding energy of its atoms. This condition governs the efficiency of a proposed light source. Hence, in particular, it follows that cluster beams formed during the expansion of a vapour escaping from a nozzle can be used as light sources because in this case the cluster lifetime is governed by the cluster transit time in the source and is short compared with the characteristic radiative times. For this reason the contribution of the emission of radiation to the heat balance of a vapour expanding beyond a nozzle is relatively small.



Figure 16. Photoabsorption cross sections of sodium cluster ions [134]: (a) Na_{45}^{+} (b) Na_{41}^{+} ; (c) Na_{44}^{+} .

Therefore, a cluster light source should be constructed on the basis of the following principles. The zone of cluster generation should be separate from the zone of light emission. A cell must be constructed in which the temperature distribution is inhomogeneous: clusters are formed in a cold zone and are directed to a hot zone where they emit and evaporate. The vapourised atomic vapour returns to the cold zone. Obviously, it is convenient to use cluster ions for two reasons. First, clusters act as the condensation nuclei; second, it is easier to control ions and direct them to the hot zone by an electric field. If such a light source is made (for the sake of simplicity) in the form of a cylindrical tube, then such a device should have the following schematic form. A high temperature is maintained at the centre of the tube, but at the peripheries a vapour is converted into ions, which are then directed to the centre of the tube in a buffer gas under the influence of an external field. During their motion these ions are converted into cluster ions, which reach the hot zone, where they emit radiation and evaporate. The atomic vapour is returned to the cold zone. This creates an inhomogeneous distribution of the vapour across the tube cross section and this distribution is governed by the balance between the flux of cluster ions to the centre under the influence of the electric field and the diffusion of atoms in the buffer gas to the cold region, where the density of atoms is lower. Such circulation ensures that each atom in the vapour is displaced repeatedly within cluster



Figure 17. Photoabsorption cross sections of large potassium cluster ions [130]: (a) K_{500}^+ ; (b) K_{900}^+ .

ions towards the centre of the tube and in the free state towards the tube walls.

We can also employ a simpler configuration in which a beam of cluster ions is generated in the cold zone and directed to the hot zone, where it emits in such a way that the cluster atoms are used only once. This method is less effective than that discussed above and it requires that the time spent by clusters in the hot zone should be sufficiently long.

We shall now consider the capabilities, in principle, of such a system and make the relevant estimates for tungsten, for which the necessary parameters have been deter-mined up to $\sim 3600 \text{ K}$ [84]. Table 9 gives the corresponding parameters of a cluster containing 10^4 atoms (its radius is 3.3 nm), although the ratio of the time constants of the processes is independent of the cluster size on the basis of

Table 9. Radiative parameters of a tungsten cluster containing 10^4 atoms and located in a hot buffer gas.

	Temperature/K				
	3400	3600	4000	4400	
Evaporation time/ 10^{-3} s	0.2	0.003	0.0003	3×10^{-4}	
Radiative time $/10^{-4}$ s	3	2	1	0.8	
Colour temperature/K	4400	4700	5300	5700	
Luminous efficiency ^a / $lm W^{-1}$	61	68	79	88	

^a Determined on the basis of the colour temperature

the models discussed earlier. The evaporation time of a cluster at a given temperature is calculated from the solution of Eqn (3.25) in which the condensation is ignored.

The parameters of the evaporation flux near a macroscopic surface are taken from Ref. [84]. The radiation emission time is the time during which the emitted energy becomes equal to the binding energy of atoms in a cluster. If this time is short, then the formation of clusters is preferable from the point of view of the energy in a light source, even if the clusters are used once. In estimates we shall use the model of a grey cluster (4.10) with the parameter $\sigma_0 = 3 \times 10^{-18} \text{ cm}^2$, which agrees with the data given in Table 9. It corresponds to the parameter f = 1.7 for tungsten.

In an analysis of the results presented in Table 9 we may reach the conclusion that a light source based on cluster ions is unpromising. Such a light source can be constructed by directing a beam of cluster ions into the hot zone, i.e. the light emission zone, in the case of single and multiple utilisation of the vapour atoms as the cluster ions. If the motion of ions in a buffer gas is controlled by an electric field and is related to it through the ion mobility, the process of transporting cluster ions may last for a fairly long time, so that the lifetimes of clusters are governed by the evaporation time in the hot zone and not by displacement time. A source of this kind is characterised by the high quality of the emitted radiation in view of its high temperature and because the radiation is emitted by all the atoms in clusters. Moreover, in accordance with this parameter, such a source is better than a lamp with an incandescent wire. Therefore, a light source based on clusters is promising. Although it is much more complex than many other existing light sources and its construction will require additional information on clusters, a source of this kind may have better output parameters.

5. Growth of clusters in an expanding gas

5.1 Formation of molecules in an expanding atomic gas

Condensation in an expanding gas or vapour is a nonequilibrium process. The nature of this process depends on the relationship between the expansion and cluster-formation times. In particular, if the density of a vapour or a gas is low, it expands before the compensation takes place in the interior, so that a beam of an atomic gas is obtained at the exit. The influence of these times on the nature of the process is easiest to consider when molecules are formed in an expanding atomic beam. If such a system consists of a single compo-nent (including the part inside the buffer gas), the process represents the first stage of cluster formation and we can understand the relationship governing the process. In the plasma-chemical method when some compound is converted into a one-component system (for example, Ti from TiCl₄), the decomposition of this compound in a plasmotron, and the later release of the dissociated component into the buffer gas or into vacuum, makes the process of formation of molecules competitive with the main process of the condensation of one of the components (metal) on ions.

We shall assume that the formation of molecules during the expansion of a gas is the result of the three-body collision of atoms:

$$A + B + C \longrightarrow AB + C$$
.

(5.1)

We shall analyse this process in order to obtain information on its rate constant. We shall begin with general comments about the process in question. Since the atomic particles A, B, and C are in this case atoms, long-lived spontaneously decaying states of molecules are not formed and the mechanism of the process is in agreement with the Thomson theory (see, for example, Refs [137, 138]). An AB molecule then forms as a result of the simultaneous collision of three atoms. The third atom, C, carries away the excess energy, so that the atoms A and B form a bound state and the binding energy is of the order of the thermal energy T of the colliding atoms. Therefore, the process can occur in a certain range of distances, of the order of b, between the atoms A and B and the critical size is given by the relationship U(b) = T, where U(R) is the potential of the interaction of the atoms A and B. The rate constant of the three-body process has the dimensions of $cm^6 s^{-1}$ and can be estimated from

$$K \propto v\sigma b^3$$
, (5.2)

where v is a typical velocity of the colliding atoms, and σ is the cross section for an elastic collision of the atom C with the atom A or B, which is accompanied by an exchange of energy of the order of T.

In particular, if the long-range interaction between atoms is described by the van der Waals potential, $U \propto R^{-6}$, the temperature dependence of the rate constant of the three-body process is

$$K \propto T^{-1/3} \tag{5.3}$$

This dependence is fairly weak against the background of the errors involved in estimating this quantity. Therefore, in simple estimates of the rate constant of the three-body process its temperature dependence can be ignored.

We do not have sufficient information on the rate constants of the three-body process involving the atoms of interest to us in the relevant temperature range. However, understanding of the nature of this process helps one to approach correctly the task of estimating its rate con- stant. Since in view of the simple structure of the colliding particles, the association of atoms is governed by the simultaneous elastic collisions of three atoms, the rate constant of the process depends weakly on temperature and on the nature of the colliding partners. This is demonstrated in Table 10, which lists the rate constants of the formation of chlorine and nitrogen molecules by three-body collisions at room temperature [139]. It follows from this table that the average rate constant of the

Table 10. Rate constants of the process $2A + C \rightarrow A_2 + C$ at room temperature [139].

А	С	$K/10^{-32} \mathrm{cm}^6 \mathrm{s}^{-1}$
Cl	Cl ₂	5.6
C1	He	3.9
C1	Ar	1.2
C1	N ₂	4.1
Ν	Ν	2.2
Ν	N ₂	1.5
Ν	He	2.2
Ν	Ar	0.93

 $2Cl + A \rightarrow Cl_2 + A$ process is $3.2 \times 10^{\pm 0.3}$ (in units of $10^{-32} \text{ cm}^6 \text{ s}^{-1}$), the rate constant of the process $2N + A \rightarrow N_2 + A$ is $1.6 \times 10^{\pm 0.2}$, and the average value that allows for both processes is $2 \times 10^{\pm 0.3}$. Since later we shall consider higher temperatures at which this process takes place, we shall use the average value of the rate

$$K = 1 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1} \times 10^{\pm 0.3}$$
 (5.4)

constant of the process:

Next, we shall determine the fraction of the molecules which are formed from an atomic vapour during its cooling when the rates of cooling and expansion of the vapour are high under nonequilibrium conditions. For simplicity, we shall consider only the model process

$$3A \xrightarrow{\longrightarrow} A_2 + A$$
 (5.5)

and determine the fraction of atoms that are converted into molecules by rapid expansion of the mixture if initially there are no molecules in a hot gas. Since the analysis is qualitative and we are interested in how the evolution of the whole process depends on the relationship between the time constants of the individual processes, we shall assume for simplicity that the fraction of molecules in the final stage is small. The equation for the balance of the number density of molecules $N_{\rm m}$ in accordance with the scheme (5.1) is

$$\frac{\mathrm{d}N_{\mathrm{m}}}{\mathrm{d}t} = -k_{\mathrm{diss}}N_{\mathrm{m}}N_{\mathrm{a}} + KN_{\mathrm{a}}^{3} , \qquad (5.6)$$

where N_a is the number density of atoms, $k_{diss}(T)$ is the rate constant of the dissociation of the molecules owing to collisions with atoms, and K is the rate constant of the formation of molecules by three-body collisions of atoms.

Under equilibrium conditions it follows from the Saha formula that $N_{
m a}^2/N_{
m m}\propto \exp(-D/T)$, where D is the dissociation energy of a molecule. Hence, $k_{\rm diss}/K \propto$ $\exp(-D/T) \propto \exp(-\gamma t)$, where $\gamma = |dT/dt|D/T^2$ ². The dissociation rate constant therefore decreases exponentially with time. Against this background we shall ignore the dependence K(t). Next, since the number density of molecules is low, the process of formation of molecules does not affect the number density of atoms. We shall assume that the number density of atoms in $N_a = N_0 \exp(-vt)$, where the parameter v is governed by the gas expansion rate and its value is $v \ll \gamma$. The parameter v is related to the gas expansion time τ_{ex} used earlier: $v = 1/\tau_{\rm ex}$.

On the basis of the above, Eqn (5.6) becomes

$$\frac{dN_{\rm m}}{dt} = -k_{\rm diss}^0 N_{\rm m} N_0 \exp[-(\gamma + \nu)t] + K N_0^3 \exp(-3\nu t) - \nu N_{\rm m} \quad .$$
(5.7)

Here, k_{diss}^0 is the initial value of the dissociation rate constant and N_0 is the initial number density of atoms. The last term on the right allows for the gas expansion.

Let us now analyse the nature of the evolution of the system described by Eqn (5.7). Initially, the rate at which equilibrium is established is described by Eqn (5.5). At the beginning this rate, described by Eqn (5.5), greatly exceeds the gas expansion rate $k_{diss}^0 \gg v$. Therefore, during the first stage of the evolution of the system the density of molecules is the equilibrium value at a given temperature, which corresponds to the solution of Eqn (5.7) by neglect of its left-hand part. During the subsequent evolution of the

system the rate of establishment of the dissociation equilibrium falls exponentially with time and the equilibrium is lost when the time needed to establish it becomes comparable to the gas expansion time. When this happens the process of formation of molecules is weakened, so that the density of molecules does not vary with time during the subsequent expansion. It is therefore convenient to rewrite Eqn (5.7) in terms of the relative proportion of molecules $c_m = N_m/N_a = N_m \exp(vt)/N_0$:

$$\frac{\mathrm{d}c_{\mathrm{m}}}{\mathrm{d}t} = -k_{\mathrm{diss}}^0 c_{\mathrm{m}} N_0 \exp\left[-(\gamma + \nu)t\right] + K N_0^2 \exp\left(-2\nu t\right) \ .$$

The asymptotic solution of this equation subject to the inequalities $k_{diss}^0 N_0 \ge \gamma \ge \nu$ is

$$c_{\rm m}(\infty) = \frac{KN_0^2}{2\nu} \left(\frac{k_{\rm diss}^0 N_0}{\gamma + \nu}\right)^{2\nu/(\gamma + \nu)} . \tag{5.8}$$

The second factor on the right-hand side of Eqn (5.8) is always smaller than unity, and its dependence on the parameters of the problem is weak. It allows for the fact that the molecules form mainly at the moment when the characteristic times of the processes become comparable and the relative fraction of the molecules which are formed is proportional to the square of the number density of atoms N_a^2 at that moment. The small parameter of the problem is therefore KN_a^2/v . This is obtained by bearing in mind that $v = d \ln N/dt \propto d \ln T/dt$ and $\gamma \approx (D/T) d \ln T/dt$, i.e. $\gamma \ge v$.

The results obtained allow us to draw conclusions about the nature of the process of formation of molecules in an expanding gas. If the number density of atoms is low, molecules cannot form and this is even more true of the condensation, because the expansion of the gas is faster than the processes of the association of atoms. It follows that the investigated condensation processes in an expanding gas and in a plasma occur at relatively high gas pressures or relatively low expansion rates.

5.2 Cluster evolution in an expanding ionised gas

The balance equations obtained above can be used to analyse the nature of the evolution of an expanding plasma in the course of the formation and growth of clusters. We shall later make this analysis for an expanding ionised gas, bearing in mind that only charged clusters can grow during the condensation process, i.e. that ions are the condensation nuclei. Under the optimal condensation conditions the cluster ions then contain a large number of atoms $\overline{q} \ge 1$. We shall assume that this condition applies to the process itself. Moreover, we shall specifically consider the parameters of a laser copper plasma.

A comparison of the balance equations (3.26) and (3.31) shows that the contribution of coagulation to the cluster growth is slight. In fact, this is true if

$$(N - N_{\text{sat}})N_{\text{c}}^{-1} \gg k_{\text{rec}}k_0^{-1}\bar{q}^{-1/6}$$
 (5.9)

It follows from the data in Table 3 that, in accordance with the above condition, the number density of atoms in a plasma should exceed by four orders of magnitude the number density of ions, which is indeed true in view of the weak ionisation of the plasma. Hence, dividing Eqn (2.32) by (3.26), we find the nature of the changes in the number density of cluster ions during their growth:

$$\frac{\mathrm{d}N_{+}}{\mathrm{d}\bar{q}} = -\frac{\kappa N_{+}^{2}}{\bar{q}^{5/6}}, \quad \kappa = \frac{k_{\mathrm{rec}}}{k_{0}N_{\mathrm{c}}} \ . \tag{5.10}$$

The solution of this equation gives

$$N_{+} = \frac{N_0}{1 + 6\kappa N_0 \bar{q}^{1/6}} , \qquad (5.11)$$

where N_0 is the number density of charged particles before the onset of condensation. We can see that the nature of the evolution of ions depends on the magnitude of the parameter $\beta = 6\kappa N_0 \bar{q}^{1/6}$. If $\beta \ge 1$, the number density of cluster ions when the condensation is complete is independent of the initial density. Table 5 gives the values of this parameter for the investigated regimes of the evolution of a laser copper plasma, and also other evolution parameters of a laser plasma obtained on the assumption that the dissociative recombination coefficient of electrons and copper molecular ions is zero.

Let us consider the evolution of large clusters. It follows from Eqns (2.31) and (2.35) that the balance equation for the number density of neutral clusters N_n is

$$\frac{\mathrm{d}N_{\mathrm{n}}}{\mathrm{d}t} = k_{\mathrm{rec}} N_{+}^{2} \bar{q}^{-1/6} - k_{\mathrm{coag}} N_{\mathrm{n}}^{2} \bar{q}^{1/6} \quad .$$
(5.12)

Estimates show that in this regime the coagulation of neutral clusters is unimportant, so that Eqns (3.22) and (3.11) yield

$$\frac{\mathrm{d}N_{\mathrm{n}}}{\mathrm{d}\bar{q}} = \frac{k_{\mathrm{rec}}N_{+}^{2}}{k_{0}N_{\mathrm{c}}\bar{q}^{5/6}} \ . \tag{5.13}$$

The approximate solution of this equation is

$$N_{\rm n} = \frac{6k_{\rm rec} N_+^2 \bar{q}^{1/6}}{k_0 N_{\rm c}} = 6\kappa N_+^2 \bar{q}^{1/6} \ . \tag{5.14}$$

Let us consider the specific case of the evolution of the system under investigation, which leads finally to the conversion of all the evaporated material into clusters. This case is of special interest in applications. The condensation time is then not very long so that the whole of the evaporated material, forming during the first stage a beam of atoms with a small admixture of charged particles, becomes converted into clusters in the final stage and the clusters are mainly charged. The average number of atoms in a cluster \bar{q} is then related to the final number density of clusters N_{+} and the initial number density of atoms N_{c} by

$$(N_{\rm n} + 2N_{\rm +})\bar{q} = N_{\rm c} \quad , \tag{5.15}$$

and the characteristic condensation time deduced from Eqn (3.26) is

$$t_{\rm c} = \frac{3\bar{q}^{1/3}}{k_0 N_{\rm c}} \ . \tag{5.16}$$

Table 5 gives the values of the parameters for the investigated laser copper plasma deduced within the framework of the adopted model. An analysis of these values shows that the assumptions made are obeyed qualitatively. Moreover, Table 5 gives the values of the parameter e^2r_0/T (r_0 is the radius of the resultant cluster), which is assumed to be small within the framework of the simplified version (2.22). We can see that it is more correct to assume the smallness of this parameter by replacing Eqn (2.22) for the cross section describing collisions of positive and negative ions with Eqn (2.33).

This analysis makes it possible to construct a physical picture of the investigated process, which is as follows. The plasma expansion and cooling results in the condensation of vapour atoms on ions. The evaporated material, which consists mainly of atoms during the first stage of the process, is in the form of cluster ions at the last stage.

5.3 Kinetics of condensation processes in a cooling gas

We have analysed the nature of condensation in an expanding ionised gas when the condensation occurs only on ions acting as the condensation nuclei and involves the attachment and evaporation of just one atom. Then, under favourable conditions, all the atoms become attached to ions, so that the whole of the atomic vapour is converted into charged clusters. Since the processes of coagulation involving the resultant clusters are not very effective under the investigated conditions, the concentration of neutral clusters at the final stage of the process is relatively low.

This regime describes the evolution of a laser plasma formed as a result of irradiating a surface. The concentration of ions in such a system is governed by the processes of evaporation of the irradiated surface and the subsequent evolution of an expanding ionised gas. This concentration is relatively low and determines the nature of the subsequent condensation processes. Generation of an expanding beam of atoms alters the conditions of condensation in the sources of beams. The temperature in the source is lower than the temperature of the laser-irradiated surface, so that there are practically no ions in the expand-ing atomic beam. Ions may be generated later and they may accelerate the process of beam clusterisation. An analysis of the processes occuring in the beam makes it possible to select the optimal distance from a nozzle for clusterisation. However, even in the absence of ionisation, beam clusterisation occurs at neutral particles, because the vapour in the beam is strongly supersaturated.

Let us consider the condensation involving neutral particles when a dense atomic beam expands and cools. In addition to the attachment and evaporation of single atoms, let us consider the merging and decay of clusters in various channels:

$$A_{l} + A_{m} \underset{v(l,m)}{\overset{k(l,m)}{\longleftrightarrow}} A_{l+m} , \qquad (5.17)$$

where v(l,m) is the decay frequency of a cluster containing m + 1 atoms into two clusters with m and l atoms and k(l,m) is the rate constant of coagulation of two clusters, which is related to the decay frequency v(l,m) of a cluster containing m + l atoms into two clusters m and l (including the evaporation of one atom) by the principle of detailed equilibrium:

$$\frac{v(l, m)}{k(l, m)} = \frac{N_l^{\rm eq} N_m^{\rm eq}}{N_{l+m}^{\rm eq}} \exp\left(\frac{-E_{\rm surf}^l - E_{\rm surf}^m + E_{\rm surf}^{l+m}}{T}\right) , \quad (5.18)$$

where the index eq means that the number densities of clusters correspond to thermodynamic equilibrium and are therefore given by Eqn (3.15). The quantity $N_{\rm sat}(T)$ in Eqn (5.18) is the saturated vapour density at a given temperature and $E_{\rm surf}^q$ is the surface energy of a cluster containing q atoms.

The balance equation for the density of clusters in accordance with the scheme (5.17) is

$$\frac{\partial f(q, t)}{\partial t} = -f(q, t)\tau_{ex}^{-1} - \alpha f(q, t) + \sum_{p=1}^{q-1} k(q-p, p)f(q-p, t)f(p, t) -f(q, t) \sum_{p=1}^{q-1} v(q-p, p) - f(q, t) \sum_{p=1}^{\infty} k(q, p)f(p, t) + \sum_{p=1}^{\infty} f(p+q, t)v(p, q) .$$
(5.19)

The first term on the right-hand side of the above equation allows for the expansion of a gas in the course of its evolution and τ_{ex} is the gas expansion time. The second term on the right takes account of the method of normalisation of the cluster distribution function. If this function is normalised to the number density of clusters N_{cl} ,

$$\sum_{q=1}^{\infty} f(q, t) = N_{\rm cl} \quad , \tag{5.20}$$

the second term is absent $(\alpha = 0)$.

We shall use the system of equations (5.19) to consider the evolution of an ionised gas discussed in the preceding subsection, when the condensation occurs on ions and results in the formation of large charged clusters and the processes of coagulation during collisions of charged clusters are unimportant. The system then has two components: atoms and large charged clusters. We shall assume that the gas expansion does not affect the nature of the evolution of the system and we shall ignore the coagulation processes, i.e. we shall limit our discussion to the scheme given by Eqn (3.6). Then, multiplication of the balance equation (5.19) by q and summation over q, gives

$$\frac{\mathrm{d}}{\mathrm{d}t} \sum_{q=2}^{\infty} qf(q, t) = \sum_{q=1}^{\infty} f(q, t) \kappa_q \left[N - N_{\mathrm{sat}}(T) \exp\left(-\frac{\Delta\varepsilon_q}{T}\right) \right],$$
(5.21)

where $\kappa_q = k(1, q - 1)$ and $\Delta \varepsilon_q = E_{surf}(q + 1) - E_{surf}(q)$ = $\varepsilon_q - \varepsilon_{sub}$. It is assumed here that large values of the number of atoms in a cluster q dominate the distribution of clusters in terms of q and that the number density of free atoms N may be related in any way to the number density of atoms in clusters $\overline{q}N_{cl} = \sum qf(q, t)$.

If the width of the distribution function of clusters in terms of the number of atoms they contain is considerably less than \overline{q} , which is the average number of atoms in a cluster, Eqn (5.21) can be written as follows:

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = N_{\mathrm{i}}\frac{\mathrm{d}\bar{q}}{\mathrm{d}t} = N_{\mathrm{i}}\kappa_{\bar{q}}\left[N - N_{\mathrm{sat}}(T)\exp\left(-\frac{\Delta\varepsilon_{\bar{q}}}{T}\right)\right] \ . (5.22)$$

Here, N_i is the number density of ions that are condensation nuclei. The changes in the number densities of atoms and clusters as a result of the gas expansion are ignored and the density of ions N_i is assumed to remain constant in time. This gives $\sum qN_q + N = \overline{q}N_i + N = \text{const.}$ Eqn (5.22) is identical with Eqn (3.25) when a suitable selection is made of the rate constant of the process and the averaging is carried out over the distribution of clusters in terms of the number of atoms in a cluster. This comparison allows us to understand better the conditions which correspond to the investigated nature of the evolution of cluster ions. Let us now consider the nature of growth of neutral clusters in the course of the expansion and cooling of a neutral gas. Then under thermodynamic equilibrium conditions the distribution function of clusters in terms of the number of atoms each contains has a minimum at the critical number of atoms in a cluster q_{cr} , which is given by Eqn (3.13). A typical condensation time at a given temperature is inversely proportional to the distribution function of clusters (3.15) at its minimum and is fairly large.

This is also true when a gas or a vapour expands in space, but the manifestation of this relationship is somewhat different. As a vapour expands and cools, the degree of its supersaturation increases and the value of the supersaturation factor of Eqn (3.8) reaches hundreds. The critical size of a cluster decreases correspondingly. The processes of attachment of atoms to clusters whose size exceeds the critical value are more effective than the evaporation processes. Therefore, such clusters grow quite effectively and their number rises strongly with increase in the degree of supersaturation of the vapour. In the final stage of this process the possibility of formation of large clusters depends on the cluster growth and gas expansion rates.

Since the cluster growth rate is proportional to the initial number density of atoms in a gas, the results of expansion of a neutral atomic gas in space depend on its initial density and on the expansion time. If the initial number density of atoms in a gas is low, then the scheme considered in Section 5.1 applies. The final product contains an atomic gas with a small admixture of molecules and the proportion of molecules increases with the initial density of the gas atoms. At high number densities of atoms in a gas the final product is in the form of clusters whose dimensions increase with the initial number density of gas atoms and with the expansion time.

Let us consider an asymptotic regime of cluster formation when the clusters are sufficiently large and the nature of the growth is described by the scheme given in Eqn (5.17). We can then ignore the evaporation compared with the coagulation. If the liquid drop model is applied to clusters, the growth of clusters by coagulation is described by Eqn (5.19) and the balance equation for the cluster density is given by the following Boltzmann equation:

$$\frac{\partial f(q, t)}{\partial t} = -f(q, t)\tau_{\text{ex}}^{-1} - \alpha f(q, t) + \int k(q_1, q - q_1)f(q - q_1, t)f(q_1, t) \,\mathrm{d}q_1 -f(q, t) \int k(q, q_1)f(q_1, t) \,\mathrm{d}q_1 \quad .$$
(5.23)

Here, $k(q_1, q_2)$ is the rate constant of coagulation of two colliding clusters containing q_1 and q_2 atoms, respectively. Moreover, the distribution function f(q, t) is normalised by the condition

$$N = \int qf(q, t) \,\mathrm{d}q \quad , \tag{5.24}$$

where N is the total number density of atoms in clusters. The parameter α in Eqn (5.23) can be deduced from the normalisation condition (5.24). We shall find this parameter on the assumption that $\tau_{ex} = 0$, i.e. we shall assume that the total number density of free and bound atoms remains constant in time. Then, multiplication of

Eqn (5.23) by q and integration with respect to q gives, on the basis of the above condition, the product

$$\alpha N = \int \frac{q_1 + q_2}{2} f(q_1, t) f(q_2, t) \, \mathrm{d}q_1 \, \mathrm{d}q_2 \ . \tag{5.25}$$

For an arbitrary value of τ_{ex} the resultant equation assumes the form

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\frac{N}{\tau_{\mathrm{ex}}} , \qquad (5.26)$$

and has the following solution:

$$\mathbf{N} = N_0 \exp\left(-\frac{t}{\tau_{\rm ex}}\right) \ . \tag{5.27}$$

Multiplication of Eqn (5.23) by q^2 and integration with respect to q yields

$$\frac{\mathrm{d}}{\mathrm{d}t} \left[\int q^2 f(q, t) \,\mathrm{d}q \left(\int q f(q, t) \,\mathrm{d}q \right)^{-1} \right]$$

= $\int \left[\frac{(q_1 + q_2)^2}{2} + q_1 q_2 - \frac{1}{2} \alpha(q_1 + q_2) \right] f(q_1, t) f(q_2, t) \,\mathrm{d}q_1 \,\mathrm{d}q_2 \,.$ (5.28)

We shall use this equation later to describe cluster evolution.

Let us calculate the rate constant of coagulation of two colliding clusters with soft surfaces:

$$\mathbf{A}_{q_1} + \mathbf{A}_{q_2} \longrightarrow \mathbf{A}_{q_1 + q_2} \quad . \tag{5.29}$$

If the clusters are spherical and their density ρ is equal to the density of a macroscopic system of bound atoms ρ , the rate constant for the coagulation of two clusters deduced from Eqn (2.35) is

$$k(q_1, q_2) = \pi (r_1 + r_2)^2 \left(\frac{8T}{\pi\mu}\right)^{1/2}$$

= $k_0 (q_1^{1/3} + q_2^{1/3})^2 (q_1 + q_2)^{1/2} q_1^{-1/2} q_2^{-1/2}$, (5.30)

where the rate constant k_0 is given by Eqn (3.27):

$$k_0 = \pi \left(\frac{3m}{4\pi\rho}\right)^{2/3} \left(\frac{8T}{\pi m}\right)^{1/2} = 1.93T^{1/2}m^{1/6}\rho^{-2/3} .$$
 (5.31)

Here, r_1 and r_2 are the radii of the colliding clusters containing q_1 and q_2 atoms, respectively; *m* is the mass of an atom; ρ is the density of the macroscopic system; the radius $(3m/4\pi\rho)^{1/3}$ corresponds to a single atom; and μ is the reduced mass of the colliding clusters. This expression is based on the liquid drop model of a cluster and will be used later to analyse the nature of cluster growth in an expanding gas.

We shall use the simplest cluster size distribution function [compare with Eqn (2.26)]:

$$f(q,t) = N_0 \exp\left(-\frac{q}{\bar{q}}\right) \left(\frac{1}{\bar{q}^2}\right) , \qquad (5.32)$$

where $\overline{q}(t)$ is the average number of atoms in clusters at a given moment. The use of Eqns (5.32) and (5.30) reduces Eqn (5.28) to

$$\frac{\mathrm{d}\bar{q}}{\mathrm{d}t} = 8k_0\bar{q}^{1/6}N \ . \tag{5.33}$$

The solution of Eqn (5.33) that allows for the nature of a change in the density of atoms in clusters of Eqn (5.27)

leads to the following expression for the average number of atoms in clusters at the end of the process:

$$\bar{q} = 10(k_0 N_0 \tau_{\rm ex})^{6/5}, \quad \bar{q} \ge 1$$
 (5.34)

Eqn (5.34) is an asymptotic expression for the average number of atoms in clusters, which is valid if there is a small parameter

$$N_0 k_0 \tau_{\rm ex} \gg 1 \quad . \tag{5.35}$$

Subject to this condition the cluster growth time exceeds greatly the gas evaporation time, which justifies the use of asymptotic relationships between the parameters. Application of the liquid drop model to a cluster is made with refer-ence to the fact (see Section 3.4) that the decay of a large excited cluster, formed by coagulation of two clusters, does not alter the nature of cluster growth in an expanding gas.

We shall allow for the influence of slowness of the process described by Eqn (5.5) on the nature of cluster growth. We shall introduce the fraction of gas atoms which form molecules:

$$\xi = \frac{2c_{\rm m}(\infty)}{1 + 2c_{\rm m}(\infty)} = \frac{KN_0^2 \tau_{\rm ex}}{1 + KN_0^2 \tau_{\rm ex}} .$$
 (5.36)

If only these atoms participate in the formation of clusters, we can replace N_0 in Eqn (5.34) with ξN_0 :

- 1-

$$\bar{q} = 10(k_0 N_0 \xi \tau_{\rm ex})^{6/5}, \quad \bar{q} \ge 1$$
 (5.37)

Eqn (5.37) also corresponds to a large value of the parameter $k_0N_0\tau_{ex}$, but if this parameter is not sufficiently large, the cluster growth process is limited to the first stage of Eqn (5.5). In fact, the process of Eqn (5.5) is of the threebody nature, whereas the process of Eqn (5.30) involves pairs. Therefore, the rate of the process of Eqn (5.5) is considerably less than that of Eqn (5.30) and, therefore, the former may delay the growth of clusters in an expanding gas. In the limit of very high values of the parameter $k_0N_0\tau_{ex}$, Eqns (5.34) and (5.37) become identical.

Application of the liquid drop model to a cluster is made on the assumption that any contact between two clusters is accompanied by a modification of the bonds within them and results in the formation of a stable spherical cluster. This is a simplified description of the collision of two clusters. In reality, the process is more complex for two reasons (see, for example, Refs [103, 104, 140]). First, the modification of the internal bonds in a cluster may be hindered and in any case requires a relatively long time. Second, the resultant complex may be unstable and may split into fragments before it becomes fully modified. The liquid drop model therefore does not work when collisions of two clusters of similar size are considered. The above circumstances reduce the value of the rate constant of the process compared with the corresponding liquid drop models and delays the process.

The influence of these factors can be estimated by considering the other limiting case when the processes of coagulation involving clusters are forbidden, so that transitions occur as a result of attachment and evaporation of individual atoms in accordance with the scheme described by Eqn (3.6). Then the number density of atoms falls during growth and free atoms involved in clusterisation may form as a result of decay of molecules and small clusters. Therefore, the average size of clusters at the completion of the process is small even if the density is high at the onset of the process.

This is illustrated in Figs 18-20, which give the results of calculations describing the evolution of our system under the assumed conditions [141]. Fig. 18 shows how the average size of a cluster depends on the initial number density of atoms, Fig. 19 gives the dependence of the average size of a cluster on the actual temperature during the evolution of the system, and Fig. 20 is a plot of the distribution function of clusters in terms of the number of atoms they contain at various moments during cluster growth. For large values of the initial gas density this regime, corresponding to the scheme described by Eqn (3.6), differs fundamentally from the regime corresponding to Eqn (5.37) when the coagulation of clusters is



Figure 18. Average number of atoms in a cluster plotted as a function of the temperature during expansion of a silver vapour beyond a nozzle. The initial number density of atoms is given. The initial vapour temperature is 2300 K [141].



Figure 19. Average number of atoms in a cluster after the end of the process, plotted as a function of the parameter $x = N_0 k_0 \tau_{ex}$ [141].



Figure 20. Distribution function of clusters in terms of the number of atoms in them, plotted for points a, b, and c in Fig. 18. The total number densities of clusters and atoms at a given moment are given.

described by the liquid drop model. In fact, in this regime, at the completion of the process the average number of atoms in a cluster depends weakly on the initial density of atoms, in contrast to the result given by Eqn (5.37) which corresponds to the merging of two clusters as a result of collision, in the same way as is true of liquid drops.

6. Experimental aspects of cluster formation in free jet expansion

6.1 Cluster beams in cluster physics

Supersonic expansion of a gas is the basic process in the generation of cluster beams. The beam formed in this way can have a higher intensity and a lower temperature than those generated by the effusion sources. Therefore, cluster beams formed by gas expansion are used not only for technological tasks, but also in studies of the properties of the clusters themselves when a cluster beam has to satisfy different requirements. In an analysis of these problems we shall concentrate our attention on the sources of metallic clusters and begin with a description of the sources of cluster and cluster ions which are used in the determination of the cluster parameters.

Two types of vapour sources are used in the formation of metallic clusters. In the case of alkali metals and a number of transition metals the vapour is generated in an oven or in a heated crucible, which is followed by the injection of a buffer gas stream, usually helium. The subsequent passage through a nozzle and expansion of this beam in vacuum leads to the formation of metallic clusters [142-146]. Metal evaporation is used for the majority of transition metals. A typical experimental setup used this purpose is shown Fig. 21 for in [147-151]. Laser radiation is usually focused on a metal wire or a disk, and the evaporated atoms enter the stream of a buffer gas, where they form clusters. The cluster size may be controlled by the parameters of the source, including the buffer gas pressure. Cluster ions of a given size are extracted from a beam by standard methods involving the use of suitable filters and mass spectrometers.



Figure 21. Apparatus used in laser generation of a beam with metallic cluster ions: (1) laser radiation used in target evaporation; (2) wire target; (3) buffer gas flow; (4) nozzle.

A metal target may be evaporated not only by laser radiation, but also by ion bombardment. Fig. 22 shows a typical arrangement used in this case [152]. Ions of a rare gas used to sputter a metal target are accelerated to 22 keV and pass through a Wien filter for purification. This filter is an ion-velocity selector. It may include a magnet and a deflecting field perpendicular to it. This technique has been used in studies of spontaneous and collisional decay of cluster ions.

Clusters and cluster ions formed by these methods can be used to analyse their various parameters, and the processes involving them. Earlier (Section 4) we considered the photoabsorption by cluster ions formed by such methods. Beams of clusters and cluster ions make it possible to measure the cluster ionisation potentials, the electron affinity of clusters, the binding energy of atoms, the excitation energies, the optical parameters of clusters, etc., providing information on clusters and cluster ions with different numbers of atoms. Fig. 23 shows schematically the apparatus used in photoelectron spectroscopy of clusters [153-155]. In this case a beam of negatively charged cluster ions forms as a result of laser irradiation of a surface and the evaporated material is carried away by a buffer gas stream, which passes through a nozzle. These negative clusters are then accelerated to energies of several hundreds of electron volts and selected by a time-of-flight mass spectrometer. The negative cluster ions with a given number of atoms are dissociated in a drift chamber under the action of laser radiation. The drift time of electrons in a strong magnetic field is determined by their energy, so that a time-of-flight spectrum of electrons gives the electron energy distribution. This method can therefore be used to determine both the binding energy of an electron in a cluster for the optimal configuration of atoms in it and the distribution of clusters in terms of the binding energy of electrons for different configurations of atoms in a cluster.

The magnetic time-of-flight photoelectron spectrometer is worth special mention, because it can be used to measure the electron energies with a satisfactory precision. The cyclotron nature of the motion of electrons in a strong magnetic field is the basis of the spectrometer [156, 157]. An electron moves freely only in the direction of the magnetic field and if its initial direction of motion is almost perpendicular to the field, the motion of an electron along the magnetic field is slow. A time-of-flight electron



Figure 22. Apparatus used in a study of fragmentation (spontaneous or collisional) of cluster ions formed by sputtering a target with a beam of rare-gas ions with kiloelectron-volt energies: (1) ion source; (2) Wien filter for ion beam purification; (3) chopper; (4) target; (5) ion optics;

(6) Wien filter for separation of cluster ions; (7) region of collisions of cluster ions with atoms or molecules of an injected gas; (8) time-of-flight reflectron for detection of cluster ions.



Figure 23. Apparatus used in generation of selective cluster beams, intended for the analysis by photoelectron spectroscopy of clusters [153 – 155]: (1) buffer gas flux; (2) laser for metal target vaporisation; (3) skimmer; (4) accelerating grids; (5) ion optics; (6) magnet; (7) laser; (8) ion detector; (9) electron detector.

spectrum can be used to determine the electron velocity along the magnetic field and hence the energy distribution of electrons.

Extensive information is available on the ionisation potentials of clusters. The dependence of the ionisation potential on the cluster size makes it possible to identify the most stable cluster structures and the corresponding magic numbers. A photoelectron spectrum of a cluster beam containing neutral clusters of different sizes can also be used to determine the magic numbers of clusters. Experiments on various modifications have been carried out for many clusters, including clusters of alkali metals and their compounds [143-145, 155-166], silver [167], copper [168], alkaline earth metals [169, 170], aluminium [170-171], indium [172, 173, 177], nickel [180], iron [181], vanadium and niobium [182], etc. These experiments have provided information both on the vertical ionisation potentials of clusters and on the mass spectra of the resultant cluster ions. Fig. 24 gives the vertical ionisation potentials of copper clusters [168].



Figure 24. Vertical ionisation potentials of copper clusters [168].

Another way of analysing the stability of clusters is based on studies of their chemical activity, which depends both on their structure and size. The chemical activity of clusters is correlated with their ionisation potentials. The relationship between the chemical activity of clusters and other cluster parameters has been studied for clusters of transition metals. Fig. 25 shows the dependence of the chemical activity of vanadium and niobium clusters, compared with that of the deuterium molecule, on the cluster size [182]; Fig. 26 shows how the growth rate constant of cluster ions, compared with that of the deuterium molecule, depends on the cluster size [183].

It should be pointed out that the problem of heat release from a beam is not so severe in the generation of a beam of ions with a given size as in the formation of a cluster beam from a beam of atoms. In fact, if a beam of cluster ions of a given size is to be used later, it is necessary to ensure that its intensity exceeds the threshold in a given experiment. Therefore, it is unimportant if the main contribution to the intensity of a beam generated in this way comes from atoms and the clusters with a given size represent the tail of the distribution function. For this reason, the conditions for generating selective cluster beams are not the same as the optimal conditions for generating intense beams, because the



Figure 25. Chemical reactivity of vanadium (a) and niobium (b) clusters with a deuterium molecule, plotted as a function of the cluster size [182].



Figure 26. Rate constants of the chemical reaction of iron clusters with deuterium molecules [183], plotted for different cluster sizes: (1) cold clusters; (2) heated clusters.

prime aim is to carry out 'clean' experiments and not to ensure a high intensity of a beam of cluster ions with a given size.

By way of example, let us consider the determination of the mobility of cluster ions of a given size in helium, which has been carried out for carbon [191], silicon [192, 193], and aluminium [194]. This example is interesting for two reasons. First, it establishes a relationship between the methods for the generation of cluster ion beams reviewed here and the measurements of the parameters of both the cluster ions themselves and the processes in which they participate. Second, it makes it possible to determine whether the liquid drop model, used above in an analysis of various processes involving clusters, is applicable to given clusters.

The method for determining the mobility of cluster ions with a given number of atoms consists of the following operations. The cluster ions are formed as a result of pulsed laser irradiation of a wire which is in continuously flowing helium. The helium is kept at a low temperature (~ 180 K), which reduces contamination and increases the output signal. The cluster ions formed in this way are focused on the entrance of a quadrupole mass spectrometer, which selects cluster ions with a given size from the beam. These ions are then focused on the entrance to a drift chamber into which they are injected with different initial energies. The ion mobility is deduced from the time of the motion of these ions in the drift chamber.

Fig. 27 gives the values of the relative mobility of a luminium cluster ions Al_q^+ with q = 5-73 at room temperature [194]. These values will be analysed later. We can see that the cluster ion mobility, considered as a function of the number of atoms in a cluster, has an oscillatory structure, which does not agree with the liquid drop model used in Ref. [194]. The degree and nature of this discrepancy of the mobility of cluster ions from the theoretical predictions is analysed in Ref. [194]. According to the liquid drop model of a cluster the process of collision of a helium atom with a cluster ion is regarded as a collision between a hard cluster whose radius is given by Eqn (3.11) and a helium atom which is a hard sphere of 0.11 nm radius. Let us denote the mobility of a cluster ion found in this way by K_0 . Fig. 28 gives the ratio of the measured mobility of a cluster ion K to this quantity at room and liquid nitrogen temperatures.



Figure 27. Relative mobility of aluminium cluster ions in helium at room temperature [194].

It follows from Fig. 28 that at some values of the number of atoms in a cluster ion the measured mobility differs greatly from the corresponding value obtained for hard spheres. This discrepancy disappears at higher temperatures. It follows that there are nonspherical cluster ion structures at low temperatures. Fig. 29 is the temperature dependence of the ratio of the mobilities measured and calculated on the basis of the spherical model, plotted for the number of atoms in a cluster when this ratio is largest. The temperature at which the ratio of these mobilities becomes unity corresponds to the energy of transformation



Figure 28. Ratio of the measured mobility of aluminium cluster ions in helium to the mobility calculated on the basis of the hard sphere model, plotted as a function of the number of atoms in a cluster at two temperatures [194].



Figure 29. Temperature dependence of the ratio of the measured mobility of Al_{45}^+ and Al_{46}^+ cluster ions in helium to that calculated on the basis of the model of hard spheres [194]. The arrows identify the temperatures corresponding to modification in the cluster structure.

 Table 11. Excitation parameters of spherical aluminium clusters [194]

 when the ground state of a cluster has a different structure.

Number of atoms in a cluster q	Excitation temperature of spherical structure/K	Activation energy/eV
27	245	0.49
45	345	0.71
46	275	0.55

from the optimal nonspherical structure to the spherical structure. The relevant data are given in Table 11 [194].

Our example thus shows how the methods for generating cluster beams from an expanding vapour or a gas can be used in specific measurements on beams of clusters of the same size. In measurements of this kind there is no need for very intense cluster beams, but 'cleaner' experimental conditions are required. Moreover, this example shows that although the liquid drop model used for clusters in this review is approximate and not always valid, on average it works quite well. The model comes closer to reality as the cluster size increases and as the temperature increases.

6.2 Experimental studies of intense cluster beams

Cluster beams are used widely in microelectronics in the fabrication of coatings and the formation of surfaces and contacts with specific properties (see, for example, Refs [10, 11, 17–28]). These beams are used in the deposition of metallic, semiconducting, and insulating films consisting of metal oxides, carbides, and halides. The cluster beam technique can be used to form organic coatings on insulating substrates [22]. The acceleration of charged clusters to high energies provides opportunities for other applications when the collisions of clusters with the surface erode it. These applications include cleaning of surfaces by the removal of a surface layer of atoms [10, 12, 195], the sputtering of a material or a change in its structure [9, 12, 195], and procedures used in thermonuclear fusion studies [29–31, 196, 197].

In all these cases the cluster beams are formed from a flux of hot atoms when the vapour escapes through a nozzle into space. The simplest source of this type is shown in Fig. 4. The processes which can occur are simpler than in the evaporation of an atomic vapour from the surface. However, in the region of formation of a beam near a nozzle the relevant parameters depend on the distances both from the nozzle and from the beam axis. These parameters have been modelled for an atomic gas [4, 198]. The velocity of a beam immediately after it is formed has the following value for an atomic gas:

$$v = \left(\frac{5T_0}{m}\right)^{1/2}$$
, (6.1)

where T_0 is the temperature in the chamber employed, *m* is the mass of a gas atom, and the asymptotic expressions for the number density of atoms *N* and the temperature *T* far from the nozzle (at a distance *x* from it) are [4, 198]

$$N = 0.15 N_0 \left(\frac{d}{x}\right)^2, \quad T = 0.282 T_0 \left(\frac{d}{x}\right)^{4/3} \quad . \tag{6.2}$$

Here, N_0 is the initial number density of atoms in the chamber, d is the nozzle diameter, and the above expressions are valid if x > 4d.

These expressions apply to an atomic gas. They should be modified when the clusterisation takes place in an atomic beam. In particular, the release of energy in the course of clusterisation alters the beam energy balance because the beam temperature is higher than that given by Eqn (6.2) even when the beam expands in the buffer gas. Moreover, the expressions in Eqn (6.2) describe the asymptotic behaviour of the beam parameters at relatively large distances (x > 4d) from the nozzle. Closer to the nozzle the distribution of the mean parameters over the cross section is inhomogeneous and it is here that the beam clusterisation takes place. One should add that the beam parameters near the nozzle depend on the nozzle profile [199].

They are slightly different for hyperbolic and straight conical nozzles [199]. All these factors complicate the theoretical analysis of the beam parameters when the clusterisation takes place.

A convenient method for analysing clusterisation in an expanding beam was developed by Hagena [13, 14, 198–202] who suggested a scaling law for a beam on the basis of the experimental data. Hagena introduced a reduced scaling condensation parameter, which will be called the Hagena parameter:

$$\Gamma^* = \frac{\Gamma}{\Gamma_{\rm ch}}, \quad \Gamma = N_0 d^q T_0^{0.25q-1.5},$$

$$\Gamma_{\rm ch} = r_{\rm ch}^{3-q} T_{\rm ch}^{0.25q-1.5}, \quad r_{\rm ch} = \left(\frac{m}{\rho}\right)^{1/3}.$$
(6.3)

Here, N_0 and T_0 are the gas parameters at the exit from the nozzle; *m* is the mass of an atom; *d* is the nozzle diameter; ρ is the density of the condensed material; and $T_{\rm ch}$ is the characteristic (species-specific) sublimation energy of a material per atom, expressed in kelvin. On average the values of *q* are within the range 0.5-1 and are selected so that the scaling law is the optimal approximation to the experimental data. The best results are obtained for q = 0.85. Table 12 lists the values of $\Gamma_{\rm ch}$ for a range of gases [201] obtained assuming this value of *q*. An analysis of various gases shows that the clusterisation occurs when $\Gamma^* > 200$.

 Table 12. Values of the Hagena reduced parameter of some vapours and gases [200].

Gas, vapour	$\Gamma_{\rm ch}/10^{14}{\rm m}^{-2.15}{\rm K}^{-1.29}$	Gas, vapour	$\Gamma_{\rm ch}/10^{14}{\rm m}^{-2.15}{\rm K}^{-1.29}$
Ar	347	Ga	5.8
Kr	210	In	5.6
Na	11.5	Ge	3.4
K	9.1	Rb	6.4
Cs	7.8	Fe	5.0
Cu	6.3	Ni	6.6
Ag	6.0	Zn	17.8
Au	4.3	Cd	16.9
Al	5.5	Hg	32.4

The Hagena reduced condensation parameter is the ratio of the rate of condensation to the rate of expansion of a beam, both obtained by a semiempirical method. Let the reduced clusterisation parameter be $x = v_{con}\tau_{ex}$, where v_{con} is the frequency of condensation (clusterisation) in a beam and τ_{ex} is the beam expansion time. The condensation (clusterisation) frequency can be found from $v_{con} = N_0 k_0$, where N_0 is the initial number density of atoms in the beam and the rate constant k_0 is given by Eqn (2.35). It then follows from Eqn (2.7) that

$$\tau_{\rm ex} = \frac{R}{u \tan \alpha} \; ,$$

where R is the beam radius, u is the beam velocity, and α is the beam aperture angle. Therefore, the dimensionless parameter representing the clusterisation in an atomic beam is

$$x = \frac{CN_0 d}{\tan \alpha} , \qquad (6.4)$$

where the constant in the case of silver is $C = 2.9 \times 10^{-16} \text{ cm}^2$. The dimensionless parameter x should obviously correspond to the Hagena parameter. In fact, the Hagena parameter is introduced as a semiempirical quantity in order to summarise the experimental results, whereas the dimensionless parameter x follows from a theoretical description of the process on the basis of the liquid drop model of clusters. The two parameters therefore represent the same process, but are based on different information on the process. It follows that if the liquid drop model of clusters used in the theoretical analysis correctly describes reality, the dimensionless parameter x should correspond to the Hagena parameter. The two parameters have similar numerical values. For example, under the conditions of Hagena's experiments [202] on the clusterisation of a beam of silver atoms ($T_0 = 2200-2400$ K, $p_0 = 18-140$ kPa, d = 0.35 - 1 mm, $\alpha = 5^\circ - 8.5^\circ$) the ratio of these parameters is

$$\frac{x}{\Gamma} = 1.0 \pm 0.2$$
 . (6.5)

This correspondence between the dimensionless parameter x and the Hagena parameter demonstrates that the liquid drop model of clusters can correctly describe the nature of the clusterisation of an atomic beam as it expands and cools after passing through a nozzle.

Let us now compare the experimental data for the clusterisation of argon with the theoretical models considered in Section 5. We shall use Eqn (5.36) for the condensed fraction and Eqn (5.39) for the average cluster size. The asymptotic expressions of Hagena [4, 198] for the parameters of a gas beyond a nozzle [see Eqn (6.2)] and the boundary conditions near the nozzle, allow us to approximate the gas parameters in the intermediate region by the following expressions:

$$T = T_0 \left[1 + 3.55 \left(\frac{x}{d} \right)^{4/3} \right]^{-1}, \quad N = N_0 \left[1 + 6.7 \left(\frac{x}{d} \right)^2 \right]^{-1},$$
(6.6)

where x is the distance from the nozzle and d is the nozzle diameter. The flow of velocity is assumed to be $v_{\rm T} = (5T/m)^{1/2}$, where m is the mass of an atom. The influence of heat release as a result of clusterisation is allowed for by replacing the initial gas temperature T_0 with the quantity $T_0 + (2\varepsilon/3)$, where ε is the binding energy of a cluster per atom. This is equivalent to the replacement of the initial kinetic energy of an atom $3T_0/2$ with $(3T_0/2) + \varepsilon$ (all the temperatures are in energy units). In particular, the initial argon temperature $T_0 = 300$ K is replaced with $T_0 = 780$ K in the case of large-cluster formation.

On the basis of the available data [139] for the rate constant of the three-body process of Eqn (5.5) (see also Table 10), we can select in accordance with Eqn (5.4) the value of $K = 1 \times 10^{32}$ cm⁶ s⁻¹, which is accurate to within a factor of 2. Fig. 30 gives the dependence of the fraction of the condensed phase on the Hagena parameter and makes it possible to estimate the validity of the assumed quantity. Fig. 31 gives the dependence of the nozzle. If the clusters on the Hagena parameter if the clusters are formed as a result of free gas expansion beyond the nozzle. If the cluster temperature is taken from Ref. [203], it follows that the clusterisation temperature is within the range 30–40 K. Then the parameter τ_{ex} should be determined at such a distance from the nozzle where the gas temperature reaches this value.

Let us now consider the results of a comparison of the experimental and theoretical data. Both theory and experiment demonstrate a strong dependence of the average size of argon clusters on the Hagena parameter, i.e. the simple model is capable of describing the main features of the process. The threshold nature of the clusterisation process is accounted for, on the basis of this model, by the small rate constant of the three-body process of formation of



Figure 30. Fraction of the condensed phase (molecules, clusters) formed on expansion of argon and xenon after passage through a nozzle, plotted as a function of the Hagena parameter. Experimental results: (1) [203]; (2) [204]; (3) [205]. Calculations based on Eqn (5.36): (4) three-body rate constant $K = 1 \times 10^{-32}$ cm⁶ s⁻¹; (5) three-body rate constant $K = 2 \times 10^{-32}$ cm⁶ s⁻¹.



Figure 31. Average number of atoms in argon clusters formed by free-jet expansion of argon from a nozzle, plotted as a function of the Hagena parameter. Experimental results: (1) [203]; (2) [206]; (3) [207]. Calculations based on Eqn (5.37): (4) three-body rate constant of formation of molecules $K = 1 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$; (5) three-body rate constant $K = 2 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$.

molecules [Eqn (5.5)], compared with the rate constant of coalescence of two liquid clusters [Eqn (5.30)]. The characteristics of this model may be included in the general

In analysing the formation of a cluster beam from a vapour source we shall assume that this vapour consists of atoms when it flows through the nozzle. The clusterisation of atoms then releases their binding energy, so that complete clusterisation of a vapour requires the presence of a buffer gas whose atoms or molecules take up the excess energy released during crystallisation. A buffer gas is used in practically all sources of cluster beams. The exception is the case of the formation of caesium cluster beams [208, 209] by electrical heating of liquid caesium with the resultant vapour flowing by a nozzle (Fig. 4). Evidently the conditions during evaporation are in this case such that the resultant vapour contains droplets. Then the clusterisation of the vapour beyond the nozzle does not result in a release of a large specific energy but leads to a redistribution of the cluster sizes.

Large clusters can be produced in the absence of a buffer gas if the surface is irradiated by a beam of ions of kiloelectron-volt energies (see, e.g. Refs [12, 152, 210–216]). Then, fragments which represent large clusters are detached from the surface. Although this method has been used to form clusters of metals and salts, the resultant cluster beams are of low intensity. When this method is used to form cluster beams, the cluster kinetics discussed above is unimportant.

7. Conclusions

The flow of a gas or a vapour into the surrounding space is a convenient method for the formation of intense cluster beams. This method involves the participation of a number of nonequilibrium processes and the nature of these processes affects the final results. Experimental investigations together with a theoretical analysis of the processes that occur have demonstrated the considerable capabilities of this method for the generation of intense cluster beams needed in various applications, and also potential improvements in the current methods used in the determination of the parameters of cluster ions and processes in which they participate. Since the transition from an expanding gas to a cluster beam is controlled by universal laws, it is natural to expect that the same processes also occur in nature, giving rise to specific natural phenomena. Moreover, understanding the processes of clusterisation in expanding beams will help in a more successful use of these beams in scientific research and in practical applications.

Acknowledgements. This work was partly supported by the National Science Foundation through a grant for the Institute of Theoretical Atomic and Molecular Physics at Harvard University and for the Smithsonian Astrophysical Observatory.

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