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Kinetic model of coupled nonequilibrium condensation and radiative excitation of water molecules

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A new microscopic kinetic model of coupled nonequilibrium condensation and radiative excitation of water molecules effusing from a surface of a cometary nucleus is developed. The method is greatly based on the microscopic theory of nonequilibrium condensation (MTC) developed earlier by the author. To analyze vibrational and rotational excitation of the H_2O molecule a kinetic model has been used which includes infrared rovibrational pumping by the solar radiation flux, thermal excitation by collisions, and radiation trapping in the rotational and rovibrational lines. Appropriate kinetic equations for cluster concentrations and populations of their energetic levels have been solved analytically. This permits one to reduce the coupled equations of the condensation and radiative balance to a closed system of differential equations involving the rotational populations of the water molecule. Prospects of the use of this model when studying an influence of the indicated processes on the structure of an inner coma are discussed. *© 1998 American Institute of Physics.* [S0021-9606(98)50807-0]

I. INTRODUCTION

This paper is the third in our series of works devoted to the investigation of nonequilibrium processes in a cometary coma and their influence on the coma structure. In the previous publications[1,2] we considered (i) a radiative excitation of the water vapor molecules evaporating from the surface of the cometary nucleus and (ii) special methods for constructing various physical and mathematical models which describe flows of a dusty gas in the coma. Such flows within the framework of the Euler approach were also explored in our paper.[3] Here we continue the study which has been started in Ref. 1 considering condensation of water vapor in the coma against a background of a radiative excitation of the water molecules.

Below we give a short review of papers where condensation and radiation in the coma were a subject of consideration. At the same time it should be emphasized that condensation in the presence of IR radiation can occur also in the earth's atmosphere or be modeled at laboratory conditions in order to manage the condensation process. Thus, although we refer to comets, the present study is addressed to a wider area of problems connected with nucleation in the presence of external radiation.

A. Condensation

Yamamoto and Ashihara[4] predicted that the expansion of water vapor effusing from the surface of a cometary nucleus and its cooling should lead to spontaneous partial condensation of H_2O into a wealth of ''water hydrates'' (or ''water clusters'') $(H_2O)_n$ $(n \gg 1)$. This process was later studied extensively by Crifo[5–9] within the framework of the classical nucleation theory (CNT).

Generally speaking, in order that spontaneous condensation induces cluster formation, a sufficient number of collisions between molecules of the condensible vapor is needed. At low vapor densities (at high Knudsen numbers) when the mean free time becomes of order of the specific gasdynamic time, some other mechanisms could also be important for the cluster formation, namely: ion-induced nucleation, photonucleation, heterogeneous nucleation on dust particles, etc. Furthermore, by virtue of chemical reactions occurring in the coma, or binary nucleation when two fugitive components could simultaneously condense into a droplet of this solution, clusters of a mixed type can be formed.

The specific mechanism of condensation depends upon various factors such as a chemical composition and a spatial structure of the nucleus and the distance of a comet from the sun. In particular, in Ref. 9 an important role of the gas production rate is emphasized because this parameter to a significant degree determines the initial Knudsen number in the vicinity of the nucleus surface. Moreover, a few competitive mechanisms of condensation could simultaneously occur. Crifo[9] studied such a mixed mechanism of water condensation in the inner cometary ionosphere (near 1 AU). The crucial effect follows from the huge water cluster's affinity for electrons and ions: they act as extremely efficient charge density traps; in other words, as long as heavy water clusters are present, the local plasma is not any more an $e^- - H_3O^+$ plasma, but a $(H_2O)_n^+ - (H_2O)_n^-$ cluster plasma. One implication is that the electric charge is, in this way, ''protected'' from the classical electron-light ion recombination: it follows that the total charge density is of about an order of magnitude more than that predicted by classical models.

Further out from the sun, it can be conjectured that spontaneous recondensation of water will yield a dominance to ion recondensation via the chain of reactions $H^+(H_2O)_n + H_2O \rightarrow H^+(H_2O)_{n+1}$. The free electrons will first recombine on $H^+(H_2O)_n$, and then attach themselves onto the neutral cluster thus produced. Therefore, qualitatively, the conclusions of Crifo valid at 1 AU should continue to hold. However, quantitative estimates made on the basis of the model[9] with allowance for spontaneous and ion-induced nucleation were not performed for the distances diverse from 1 AU.

Another example is the work[10] where a simultaneous occurrence of heterogeneous and ion-induced condensation of products of methane photodissociation in the neptune atmosphere was investigated based upon CNT.

Within this paper we consider only homogeneous spontaneous condensation of water vapor but with a number of essential differences from the models known in the literature. First, for the first time in cometary physics we use principally a more modern model of the condensation kinetics.[11,12] Second, this model is modified in order to take into account both condensation and radiative excitation of the water molecules by the solar illumination and their mutual influence.

B. Radiative processes

Radiative processes play an important role in forming the structure of inner cometary comae. As a rule, the inner coma is characterized by the low temperature of vapor evaporating from the nucleus surface and consists largely of molecules of water and dusty particles. For the water molecules a maximum of absorption and emission in the presence of the solar radiation lies in the IR region, therefore their vibrational degrees of freedom usually are not excited, as opposed to the rotational and rovibrational ones. The physical analysis of the kinetic mechanism of the water molecule excited by the solar light has been done in Refs. 13 and 14 and confirmed by the observational results of Ref. 15. Owing to a small number of the populated rovibrational levels and relatively high density of the water molecules in the coma, a certain amount of radiative lines are optically thick.[13,14] While the number of the populated levels is not too large, it is necessary to consider a sufficiently large total number of levels when studying a mechanism of the radiative excitation. By virtue of it, a usage of the exact radiative transfer equations is extremely labor consuming and special approximate analytical methods were developed which take into account the influence of the optical depth on the kinetics of the process. One of them is the escape probability method[16] originally proposed for a spherically symmetrical coma. Being applied, this method permits one to take into account the indicated influence and still remain within the framework of the balance kinetic equations in lines but with the Einstein coefficients multiplied by a certain factor which is strongly nonlinear over populations.

When modeling the water vapor flows in the inner coma with allowance for the radiative transitions because of the large dimension and essential nonlinearity of the system of the kinetic equations one usually tries to be limited by the elementary one-dimensional stationary models.[13] Recently we explored the dynamics of the water vapor expiration from the nucleus surface with allowance for the radiative processes using a one-dimensional unsteady approach.[1]

It turned out that an intensive exchange by the energy between the internal and translational degrees of freedom results in a sharp difference of the flow parameters from the adiabatic ones. In addition, during the flow evolution unsteady oscillations of the parameters' values were observed in the stream. It was revealed that the intensity of these oscillations is insufficient to produce locally subsonic zones in the initially supersonic flow. However, this could be the case if one takes into account the presence of dust particles (which decelerate the stream) or the vapor condensation (which also locally decelerates the stream because of the latent heat extraction).

Note that so far in the existing literature on cometary physics the following problem has not been raised at all, that from the physical point of view a rotationally excited molecule should be less capable to condense against a nonexcited molecule. It is hard to take this fact into account within the framework of CNT in contrast to our theory which allows one to generalize it for this case in a quite natural way. Thus within the scope of such a modified model, condensation and radiative excitation become the coupled processes that should be taken into account when elaborating an appropriate theoretical description of this phenomenon. Therefore, the main goal of this work is to present such a theory developed on the basis of our microscopic condensation theory.

The structure of the work is the following. First, we derive new kinetic equations which describe coupled condensation and radiative excitation of the water molecules. Then we propose an asymptotic method to get analytical solutions of these equations. It gives rise to the closed system of differential equations only for supersaturation S_0 and populations $x_1(k)$ of the rotational states of the water molecule. Solving this system one can further analytically restore the cluster size distribution function as well as populations of the internal states of the clusters. Finally, some new features of this solution, in particular an appearance of singularities at a certain S_0, are discussed. However, the results of simulation of water vapor flow effusing from the surface of a cometary nucleus produced with the help of the present model will be published in a separate paper.[17]

II. KINETIC EQUATIONS

Two different basic approaches exist to describe phase transitions of the first kind. The nucleation process considered here is one of the examples. The first approach is the kinetic theory of gases. Within this theory the object under investigation is an ensemble of molecules whereas the phase transition is recognized as an appearance of long-term correlations in such a system or singularities in the respective kinetic equation. Under this consideration a definition of the physical cluster should be introduced on the basis of a certain additional relation which unites together all the monomers pertaining to this cluster. In principle, it is possible to consider this approach as a consequent generalization of the basic statements of the kinetic theory for the case of the condensible system. However, this point of view has not brought any essential achievement. In view of this, in our opinion it is more feasible to concentrate on the other approach. Following its main idea the condensible gas is assumed to be a mixture of monomers, dimers, etc., i.e., from the very beginning clusters are introduced as real physical objects which exist both in stable and metastable phases. If such a statement is accepted the phase transition could be further treated as a sequence of chemical reactions providing a redistribution of molecules from small clusters to the large ones, or in other words providing an increase of concentrations of the large clusters in the process of their coalescence with both molecules and small clusters. This consideration has been used in the Szilard model and we also put it in the basis of our model used in the given work.

The subject of our study is the water vapor evaporating from the surface of a cometary nucleus affected by the solar light. We treat this stream as a mixture of ideal gases, each of which consists of the water molecules being in a certain internal state. In accordance with Ref. 13 we further consider only the processes of nonequilibrium excitation of rotational sublevels belonging to the ground vibrational state of the water molecule. Thus each of the molecular components of the mixture represents molecules of water being in a certain rotational state while excitation of the vibrational states of the water molecule assumes to be inefficient at specific temperatures on the surface of nucleus $T=100-200$ K.

In general, we introduce a cluster as a molecular complex (either a stable or unstable one) formed by hydrogen, Van der Waals, metallic, or some other types of chemical bond but we do not distinguish isomers of the cluster from each other. The internal energy of this complex can be specified as usual in the molecular physics by a set of quantum numbers corresponding to the different internal modes. Let us consider the processes of translational relaxation of molecules and clusters to be rapid enough, so that we can introduce a common translational temperature of the whole mixture T. Generally speaking, this assumption is not correct for the very large clusters, but their concentration in the system is small enough, therefore such an assumption should not affect in the least the integral characteristics of the system.

The distribution of the rotational energy of the clusters can also be accepted as an equilibrium one. To give evidence to this point we shall notice, that: (1) External radiation exciting the rotational degrees of freedom of a monomer is not effective with respect to excitation of librational oscillations of molecules inside a cluster in which rotations of free molecules are transformed when these molecules attach to the cluster. It is connected with a significant shift of frequencies in such a process owing to the external solar radiation at frequencies corresponding to a maximum of the solar spectrum intensity which becomes nonresonant to excite single-quantum rotational transitions. We shall neglect multiquantum transitions or poorly intensive excitation of single-quantum transitions. (2) Probability of the attachment of a rotational excited molecule to a cluster should be far less than that for the nonexcited one (see further). By virtue of that the cluster is formed preferably by the attachment of the rotationally nonexcited molecules.

Thus the rotational degree of freedom of the cluster as the whole can be excited basically at collisions, and principally with molecules (including rotationally excited ones) because collisions among the clusters are rather rare. However, such excitations relax practically at some mean free times. Therefore in what follows we assume that the rotational degrees of freedom of clusters can be described by the rotational temperature, and that it coincides with the rotational temperature of the mixture T which, in turn, is equal to the translational temperature of the mixture.

As far as the vibrational energy is concerned its rate of relaxation can be of the order of the rate of the formation and decay of the clusters. It is clear that even the minor complexes, trimers, tetramers, etc., can have quite a great number of the vibrational modes, therefore for the sake of simplicity it is convenient to subdivide all of them into two groups considering in a harmonic approximation. In the first one we collect vibrations of the molecules being a part of the cluster (intermolecular oscillations). In the second one we unite vibrations of atoms which form the molecule (monomer), i.e., the internal molecular vibrations. Intermolecular vibrations are low-energetic ones. For example, the specific frequencies of the Van der Waals complexes are $50-200\ \mathrm{cm}^{-1}$. But for the internal vibrations various situations are possible.

(1) If these vibrations have low frequencies they effectively exchange energy with the intermolecular vibrations that allows one to introduce the total vibrational energy of the cluster $E_j(k)$ (j is the number of molecules in the cluster, k is the number of the energetic level). At the moment the existence of the different types of intermolecular oscillations is not taken into account here. In addition, we do not consider the radiationless transitions in the process of the intermode energy exchange. All these assumptions are made in order to simplify as much as possible a very complicated picture of the redistribution of the internal energy inside the cluster, but at the same time to keep the main features of the process.

(2) If the monomer has high-frequency vibrational modes, they inefficiently interact with the intermolecular vibrations. In this case, with respect to the condensation process, the monomer behaves as a structureless particle and due to a rather high value of its vibrational quantum the excited vibrational states of the monomer are poorly populated. This situation is close to the condensation theory of monoatomic gases being a particular case of the theory developed here. Nevertheless, even for such a case the vibrational degrees of freedom of the cluster can be characterized by the value of their total energy $E_j(k)$.

To analyze kinetics of the radiative transitions of the H_2O molecule a model in Ref. 13 is used. Within the frameworks of this model, as the main processes affecting the energy redistribution among the mixture constituents and the external radiation, we take into account infrared rovibrational pumping by the solar radiation flux, thermal excitation by collisions, and radiation trapping in the rotational and rovibrational lines.

As was already mentioned when formulating the kinetic model we introduce two essential assumptions. First, excitation of the vibrational states of the water molecule assumes to be inefficient at temperatures $T=100-200$ K specific for the surface of a cometary nucleus. It is necessary to notice that such an assumption is not a restriction of MTC as in its original version intramolecular vibrations are taken into account[18,12] and only permits one to simplify the further algebra with allowance for a real physical picture of the process under investigation. Second, it is assumed that the rotationally excited molecule has a smaller cross section to be attached to the cluster than the nonexcited. This problem was theoretically investigated in Ref. 19 with the purpose to explain experiments on rotational-selective condensation of water and heavy water molecules.[20,21] A multistep mechanism of the resonant capture of molecules through the formation of an intermediate complex was considered which was illustrated by system He–H_2O. It was found in these works that the ratio η of the rate constant of capture of the water molecule being in the ground para state to the same rate constant of the water molecule being in the ground ortho state is $8.4\leqslant\eta\leqslant 12.3$ as the temperature is ranged within the limit $30\ \mathrm{K}\leqslant T\leqslant 50\ \mathrm{K}$. Thus these data testify to an opportunity of the rotational selectivity of condensation already at the stage of capture. It is clear that as the rotational energy of the molecule increases its rate constant of capture decreases. Therefore in this work we use a model where the only molecules being in a ground para state (i.e., rotationally nonexcited) are most capable to condense while the probability of the formation of molecular complexes by attaching the water molecule being in another rotational state is neglected.

Further for the sake of simplicity we consider a spatially uniform system for which parameters vary with time. Generalization of this method for a spatially nonuniform system will be given elsewhere. With allowance for the assumptions made the above kinetic equations describing an evolution of populations of rovibrational levels which belong to the ground vibrational state of the water molecule $x_1(k)$, $k=0,\ldots,M_1$ and populations of the energetic levels corresponding to intermolecular vibrations in the cluster $x_j(k)$, $k=0,\ldots,M_j$, $j=2,\ldots,N$ can be written in the form

$$
\begin{aligned}
\frac{dx_j(k)}{dt} &= \Phi_{j,k} \equiv \sum_{l=0}^{M_{j-1}} I_{j-1}(l,0|k) - \sum_{l=0}^{M_{j+1}} I_j(k,0|l)(1-\delta_{jN}) \\
&\quad + \sum_{l=0}^{M_j} \sum_{\nu=0}^{M_1} \sum_{i} J_j(l,i|k,\nu), \quad j>1, \\
\frac{dx_1(k)}{dt} &= -\sum_{j=2}^{N} \sum_{i,l=0}^{M_j} \sum_{\nu=0}^{M_1} J_j(l,k|i,\nu) + \Omega_k^c + \Omega_k^r, \quad k\neq 0, \\
\frac{dx_1(0)}{dt} &= -\sum_{j=2}^{N-1} \sum_{i=0}^{M_{j+1}} \sum_{l=0}^{M_j} I_j(l,0|i) - 2\sum_{i=0}^{M_{j+1}} I_1(0,0|i) \\
&\quad - \sum_{j=2}^{N} \sum_{i,l=0}^{M_j} \sum_{\nu=0}^{M_1} J_j(l,0|i,\nu) + \Omega_0^c + \Omega_0^r, \\
I_{j-1}(l,0|k) &= C_{j-1}(l,0|k)\overline{x_{j-1}}(l)\overline{x_1}(0) - E_j(k|0,l)\overline{x_j}(k), \\
J_j(l,i|k,\nu) &= R_j(l,i|k,\nu)\overline{x_j}(l)\overline{x_1}(i) - R_j(k,\nu|l,i)\overline{x_j}(k)\overline{x_1}(\nu), \\
\Omega_k^r &= \sum_{i'} A_{i'k}x_1(i') - x_1(k)\sum_{i'} A_{ki'} + \sum_{i'} B_{i'k}\mathscr{J}(\lambda_{i'k})x_1(i') \\
&\quad - x_1(k)\sum_{i'} B_{ki'}\mathscr{J}(\lambda_{ki'}), \\
\Omega_k^c &= C_c[\overline{x_{1e}}(k) - \overline{x_1}(k)], \quad \overline{x_j}(k) = x_j(k)/s_j(k).
\end{aligned}
\tag{1}
$$

Here the fluxes I_j describe the formation and decay of the clusters; J_j, relaxation of intermolecular vibrations in the clusters, Ω_i^c and Ω_i^r, collisional and radiative fluxes for the water molecule being in the ith rotational state. The other notation is as follows: m is the monomer's mass, $C_{j-1}(l,0|k)$ is the rate of formation of the j cluster with energy $E_j(k)$ from the $j-1$ one with energy $E_{j-1}(l)$ by attaching the monomer being in the ground rotational para state; $E_j(k,|l,0)$ is the rate of decay of the j cluster with energy $E_j(k)$ into the $j-1$ one with energy $E_{j-1}(l)$ and the monomer being in the ground rotational para state; $R_j(l,i|k,v)$ is the rate of relaxation of the j cluster from the state with energy $E_j(l)$ to the state with energy $E_j(k)$ accompanied by the simultaneous relaxation of the monomer (RT relaxation) from the state with energy $E_1(i)$ into the state with energy $E_1(v)$; M_j is the number of the topmost energetic level (see below) of the j cluster, $s_j(k)$ is the statistical weight (degeneracy) of the j cluster, δ_{ij} is the Kronecker delta, $A_{ii'}$d $B_{ii''}$ are the Einstein coefficients for spontaneous and induced radiation, $\gamma_{ii'}$ is the wavelength of the transition, $\mathscr{J}$ is the intensity of the radiative flux averaged over all the directions and integrated over the whole line, C_c is the total collision rate for rotational transitions, and x_{ie} is the equilibrium populations at the given temperature.

Further it is convenient to change the traditional MTC notation for the rate constants of formation and decay for a more compact one with allowance for the circumstance that within the present model condensation from the only ground rotational state of the water molecule is taken into account therefore index 0 is dummy. By virtue of it let us introduce new designations $\mathscr{E}_{j,Mk}\equiv E_j(M|0,k)$, $\mathscr{C}_{j,kM}\equiv C_j(k,0|M)$.

When writing Eq. (1) a model of strong collisions is used allowing us to write the collisional term in the Bathnagar–Gross–Krook (BGK or ''relaxation'') form. Coefficients A_{ij} vanish if $E_i<E_j$. Furthermore, in Eq. (1) deriving the possibility that the cluster could be formed (decayed) by gaining (losing) a dimer, trimer, etc., was neglected as well as the triple collisions of the molecules and clusters. Besides, in Eq. (1) the conservation law preserving the total number of molecules in the system is already taken into account.

$$
\sum_j \sum_k x_j(k) = \sum_j n_j = 1,
$$

where n_j is the numerical fractional concentrations of the clusters of size j.

The further program of our actions is as follows. System Eq. (1) is too complicated to be solved directly by virtue of (i) its infinite dimension (in a real system $N\to\infty$) and (ii) the absence of data on the majority of rate constants of the elementary processes considered in Eq. (1). Therefore at first we discuss asymptotic solutions obtained by using a special quasisteady-state method similar to that in Ref. 11 and given in more detail in Appendix A. Then we use another asymptotic method to obtain an explicit analytical solution for the cluster concentrations. Explicit expressions for equilibrium concentrations and populations of the clusters presented in these equations were given in Refs. 22 and 12 as well as the model rate constants of the attachment and detachment of a single molecule to the cluster (they have been obtained in Refs. 23 and 24 with the help of the statistical theory of monomolecular reactions and the microscopic reversibility).

III. ANALYTICAL SOLUTIONS OF THE KINETIC EQUATIONS

A detailed exposition of asymptotic methods developed to find analytical solutions of the equations of type Eq. (1) is given in Refs. 25, 18, 26 and 27. Here we only briefly describe the main stages of getting these solutions and assumptions made. To construct this asymptotical solution we use the general idea of the theory of the singularly perturbed system, namely: It is necessary to subdivide all variables in the studied equations; Eq. (1) into two groups, the fast and slow ones, i.e., the variables which have the substantially different characteristic times of relaxation. After that we examine the behavior of the whole system in the scale of the evolution of the slow variables. For such times the fast variables do not explicitly depend upon time but only upon the slow variables themselves (a quasisteady-state regime). If we manage to find the evident form of such a function then we could substitute it into the equations for the slow variables and derive a closed reduced system for them.

On the whole the method of finding these quasisteady solutions proposed in Refs. 18 and 26 consists of three main steps.

A. Stage 1

The initial step is connected with a substitution of variables $x_j(0)$ for concentrations n_j at all j. Equations for n_j could be found from Eq. (1) by summing the equations for $x_j(k)$ over all k.

$$\frac{dn_j}{dt}=I_{j-1}-I_j, \tag{2}$$

where $I_j=\Sigma_{l,k}I(l,0|k)$. Further it is possible to prove that all populations $x_j(k)$, $j=2,...,N$, $k=1,...,M_j$ are the fast variables with respect to the slow concentrations n_j and T.[18,12]

B. Stage 2

Having subdivided all the variables into the fast and slow ones it is further possible to use special methods of asymptotic integration for singularly perturbed ordinary differential equations, for example, a method of boundary functions.[28] A concrete realization of this idea for the kinetic equations of MTC in a general case is given in Refs. 18 and 12. The sense of previous manipulations is that for specific times of evolution of the slow variables (i.e., concentrations) the quasisteady equations for $x_j(k)$ have the form

$$\Phi_{j,k}=0, \quad k\geqslant 1, \quad j\geqslant 2. \tag{3}$$

In other words instead of the initial differential equations Eq. (1) for $x_j(k)$, we should solve a more simple system of algebraic equations, Eq. (3).

However, as already mentioned above it is without doubt the unreal problem to find the exact solution of this system. For this reason we propose a convenient approximation based on the understanding of the physical nature of the phenomena. The point is that for the large clusters with the substantially excited intracluster vibrations the rate of dissociation of the molecule from the cluster is much less than the rate of the vibrational relaxation at these levels while for the small clusters the opposite relationship could take place. In view of this it is reasonable to introduce the special cluster size r such that in its physical meaning r is the number of molecules in the cluster for which the dissociation rate from the topmost level M_r (for the detailed definition of the level M_j see below) is of the same order of magnitude as the vibrational relaxation rate at the same level. For the clusters with $j>r$ the rate of relaxation of the intracluster vibrations is much greater than the rate of the cluster dissociation but at $j<r$ there is an opposite situation. An analytical solution for the equations of the type Eq. (1) was obtained in Ref. 26 for the model of single-quantum transitions and the BGK model. Note that these solutions are valid for a rather general form of rate constants of formation, decay, and relaxation of the clusters. The result are analytical relationships which express quasisteady populations $x_j(k)$, $j\geqslant 2$ through the cluster concentrations and populations of monomers.

In our case of nonequilibrium distribution of monomers over the rotational degrees of freedom a similar solution can be obtained if one describes relaxation of intracluster vibrations in the frameworks of the BGK model (model of strong collisions). Details of this method as applied to the model of condensation in the presence of the external radiation considered in this work are given in Appendix A.

Substituting the obtained relationships for $x_j(k)$ into the equations for n_j one can get for n_j, $j\geqslant 1$, $x_1(k)$, $k=1,...,M_1$ a closed system of equations which in a general form are given in Refs. 8, 27, and 12. It turns out that if the rate of relaxation of the internal energy of monomers (for polyatomic molecules) is more than the rate of dimerization then for $j>r$ the quasisteady equations coincide with those of the quasichemical (Szilard) model. In all the other cases ($j\leqslant r$, slow relaxation of monomers) the obtained equations differ much from the agreed upon ones. For the case considered here when only condensation of water molecules being in a ground rotational para state is taken into account such equations for slow variables take the form (see Appendix A):

$$\frac{dx_1(0)}{dt}=-\sum_{k=1}^{M_1}\frac{dx_1(k)}{dt}-\sum_{j=2}^{r-1}j\,\frac{dn_j}{dt}+\frac{dn_r}{dt}$$
$$-(r+1)\hat{I}-\sum_{j=r+2}^{N-1}I_j^{(1)},$$

$$\frac{dx_1(k)}{dt}=\Omega_k^c+\Omega_k^r, \quad k\neq 0,$$

$$\frac{dn_j}{dt}=I_j^{(2)}-d_j\hat{I}, \quad j=2,...,r-1,$$

$$
\begin{aligned}
\frac{dn_r}{dt}&=\frac{n_r(1-f_r)}{\tau_r}\left[\frac{z_r(M)(1-\tau_r\theta)}{\tau_r\theta}\right.\\
&\quad\left.-\sum_{k=1}^{M-1}\frac{\mathscr{C}_{r,kM}\overline{x_1}(0)z_r(k)}{\mathscr{C}_{r,kM}\overline{x_1}(0)+\tau_r^{-1}}\right]\\
&\quad-\frac{\mathscr{E}_{r,MM}n_{re}z_r(M)}{\nu S_0\theta\tau_r}I_{r+1}^{(2)}\\
&\quad+\frac{n_rz_r(M)f_r}{\tau_r\theta}\mathscr{C}_{r,MM}n_{1e}z_1(0)(1-S_0),\\
\frac{dn_{r+1}}{dt}&=\hat{I}-I_{r+2}^{(1)}-\frac{dn_r}{dt},\\
\frac{dn_j}{dt}&=I_j^{(1)}-I_{j+1}^{(1)}(1-\delta_{jN}),\quad j>r+1.
\end{aligned}
\tag{4}
$$

Here $I_j^{(1)}$, $I_j^{(2)}$, and $\hat{I}$ are the fluxes that can be generally represented as

$$
\begin{aligned}
I_j^{(1)}&=K_j^+n_{j-1}\overline{x_1}(0)-K_j^-n_j,\\
I_j^{(2)}&=L_j^+\overline{x_1^j}(0)-L_j^-n_{j-1}\overline{x_1}(0),\\
\hat{I}&=-\frac{\mathscr{E}_{r,MM}n_{re}z_r(M)}{\nu}\left\{\frac{\overline{n_r}(1-f_r)}{\tau_r\theta}+\frac{1}{S_0}\left(\frac{\mathscr{E}_{r,MM}}{\nu\theta}-1\right)\right.\\
&\quad\left.\times I_{r+1}^{(2)}+\frac{\mathscr{C}_{r,MM}\overline{x_1}(0)}{S_0\theta}\overline{n_{r+1}}(1-S_0)\right\},
\end{aligned}
\tag{5}
$$

$f_r=\overline{n_{r+1}}/S_0\overline{n_r}$, $\overline{n_j}=n_j/n_{je}$, $S_0=\overline{x_1}(0)/n_{1e}z_1(0)$ is an analog of supersaturation and $z_j(i)$ is the Boltzmann factor (statistical weight) of the ith state of j clusters. Coefficients K_j^+, L_j^+, and K_j^-, L_j^- are the nonequilibrium rate constants describing the cluster formation and decay that depend not only upon the temperature T but also upon $x_1(k)$, $k=0,...,M$. The explicit form of all coefficients presented in Eqs. (4) and (5) is given in Appendix A. A convenience of Eq. (5) is that at equilibrium $I_j^{(i)}$, $i=1,2$ as well as $\hat{I}$ vanish.

We shall notice that when writing Eq. (4) we have kept equations for populations $x_1(k)$ in a general form and did not purposely compare the rate of relaxation of the internal energy of monomers and the rate of all the other processes. It does not contradict a general idea of the ‘‘boundary functions’’ method, however, it permits one to consider hereinafter various cases of the monomer relaxation in the frameworks of a common scheme.

C. Stage 3

To solve the derived equations for the cluster concentrations in the case of the fast relaxation of monomers in Ref. 26 we developed a special asymptotic method. Originally it was utilized in Ref. 22 to find analytical solutions of the quasichemical model but later was generalized also for MTC.[26] It allows one to obtain the analytical expression of the cluster concentrations for nearly all sizes (save the biggest ones) through supersaturation $S=n_1/n_{1e}$ and temperature T. The method is based on a nonlinear substitution of variables $n_j\to f_j$ such that the initially coupled equations for n_j in new variables could be decomposed so that each equation of this new system could be solved independently from each other (factorization). Three important assumptions are made to do that.

1. For the large clusters the following relationship is valid $\Sigma_{l,i}E_j(k|i,l)\sim j^{\nu}$, $\nu\leqslant 1$.
2. The equilibrium concentrations follow the relationship $n_{je}/n_{1e}\ll 1$.
3. At $j>r$ variables f_j smoothly depend upon j so that

$$1-\frac{f_j}{f_{j-1}}\simeq\epsilon\ll 1.$$

In Refs. 23, 24, and 12 the model expressions of rate constants for the cluster's formation and decay were obtained with the help of the statistical theory of the chemical reaction rates. As shown in Refs. 26 and 12 for such constants there is reliable evidence of these assumptions.

However, in the case of slow relaxation of monomers the common solution of the quasisteady equations for concentrations have not yet been obtained. Thus if the monomer populations may vary with an arbitrary rate to solve Eq. (4) it is necessary to develop a special asymptotic method.

In what follows we describe such a modification of the method[26] as applied to Eq. (4). Let us introduce the following substitution of variables $x_1(0),n_2,\ldots,n_N\to S_0$, $f_2,\ldots,f_{N-1}$, where

$$
\begin{aligned}
f_j&=\overline{n_{j+1}}/S_0^{j+1},\quad j=1,...,r-1,\\
f_j&=\overline{n_{j+1}}/S_0\overline{n_j},\quad j=r,\ldots,N-1,\\
S_0&=x_1(0)/n_{1e}z_1(0).
\end{aligned}
\tag{6}
$$

Further we exclude variable $x_1(M)$ from the system introducing instead concentration $n_1=\Sigma_kx_1(k)$. Thus instead of the equation for $x_1(M)$ we use the equation for n_1 which could be obtained summing all the equations for $x_1(k)$ over all k. Nevertheless, we keep $x_1(M)$ in the right-hand side (R/H/S) of these equations but now it is not a variable but a notation

$$x_1(M)=n_1-\sum_{k=0}^{M-1}x_1(k).$$

Omitting an intermediate algebra we give rise to the equations, Eq. (4) written in new variables, and the equation for $S=n_1/n_{1e}$

$$
\begin{aligned}
\frac{df_j}{d\tau}&=Y_j-(j+1)f_j\frac{d\ln S_0}{d\tau},\quad j=1,...,r-1,\\
\frac{df_r}{d\tau}&=Y_r-\left(f_r+\frac{n_{re}}{S_0n_{r+1,e}}\right)Y_{r-1}-f_r\frac{d\ln S_0}{d\tau},\\
\frac{df_j}{d\tau}&=R(f_j)-f_j\frac{d}{d\tau}\ln\left(\frac{S_0n_{j+1,e}}{n_{je}}\right)+\mu_j\\
&\quad+\delta_{j,r+1}\frac{n_{re}}{n_{r+1,e}S_0}\frac{f_{r+1}}{f_r}\left[Y_{r-1}+\frac{\overline{\gamma}}{Kn_{1e}z_1(0)}\hat{I}_u\right],\\
&\quad j=r+1,...,N-1,
\end{aligned}
$$

$$\frac{dS_0}{d\tau}=-\sum_{j=2}^{r} j\beta_j S_0^j f_{j-1}Y_{j-1}-(r+1)f_{r-1}S_0^r\beta_r\left[Y_{r-1}\right.$$
$$\left.-\frac{n_{r+1,e}S_0}{n_{re}}\,Y_r\right]-\sum_{j=r+2}^{N-1}\left[1+(r+1)\delta_{j,r+2}\right]$$
$$\times\overline{K_j^+}S_0^j\beta_{j-1}(1-f_{j-1})$$
$$\times\prod_{i=r-1}^{j-1} f_i-\frac{1}{K(n_{1e}z_1(0))^2}\sum_{k=1}^{M}(\Omega_k^c+\Omega_k^r),$$

$$\frac{1}{z_1(0)}\frac{dS}{d\tau}=-\sum_{j=2}^{r} j\beta_j S_0^j f_{j-1}Y_{j-1}-(r+1)$$
$$\times f_{r-1}S_0^r\beta_r\left[Y_{r-1}-\frac{n_{r+1,e}S_0}{n_{re}}\,Y_r\right]$$
$$-\sum_{j=r+2}^{N-1}\left[1+(r+1)\delta_{j,r+2}\right]$$
$$\times\overline{K_j^+}S_0^j\beta_{j-1}(1-f_{j-1})\prod_{i=r-1}^{j-1} f_i,$$

$$\frac{1}{n_{1e}z_1(0)}\frac{dx_1(k)}{d\tau}=\frac{1}{K(n_{1e}z_1(0))^2}(\Omega_k^c+\Omega_k^r),$$
$$k=1,\ldots,M-1. \tag{7}$$

Here Y_j are the fluxes that turn to zero at $f_j=1$.

$$Y_j=\frac{\overline{C_{j+1,0M}}S_0}{s_{j+1}(0)}\left(1-f_j+\phi_j\,\frac{f_{r-1}}{S_0\theta\tau_r}\,\hat{I}_u\right),\quad j=1,\ldots,r-2,$$

$$\phi_j=\left[\frac{\mathscr{C}_{r-1,MM}n_{r-1,e}z_{r-1}(M)}{\mathscr{C}_{j+1,MM}n_{j+1,e}z_{j+1}(M)}\right]$$
$$\times\left[\frac{1+\mathscr{C}_{j+1,MM}\overline{x_1}(0)\alpha_{j+1}}{1+\mathscr{C}_{r-1,MM}\overline{x_1}(0)\alpha_{r-1}}\right]S_0^{r-j-1},$$

$$Y_{r-1}=-\frac{\overline{\gamma}}{Kn_{1e}z_1(0)}(1-f_{r-1}f_r)$$
$$+\frac{\gamma_1}{Kn_{1e}z_1(0)}(1-f_r)f_{r-1}$$
$$+\frac{f_{r-1}f_r}{\tau_r\theta}\overline{\mathscr{C}}_{r,MM}z_r(M)(1-S_0),$$

$$\overline{\gamma}=\frac{\mathscr{E}_{r,MM}z_r(M)}{\nu\theta\tau_r},$$

$$\gamma_1=\frac{1}{\tau_r}\left[\frac{z_r(M)(1-\tau_r\theta)}{\tau_r\theta}\right.$$
$$\left.-\sum_{k=1}^{M-1} z_r(k)\frac{\mathscr{C}_{r,kM}\overline{x_1}(0)}{\mathscr{C}_{r,kM}\overline{x_1}(0)+\tau_r^{-1}}\right],$$

$$Y_r=-\frac{\overline{\gamma}}{Kn_{1e}z_1(0)}\frac{n_{re}}{S_0n_{r+1,e}}\hat{I}_u-\overline{K_{r+2}^+}S_0f_r(1-f_{r+1}),$$

$$\hat{I}_u=-\theta\tau_r\left(1-\frac{\mathscr{E}_{r,MM}}{\nu\theta}\right)\frac{1-f_rf_{r-1}}{f_{r-1}}+1-f_r$$
$$+\tau_rf_r\mathscr{C}_{r,MM}n_{1e}z_1(0)(1-S_0).$$

The bar over the parameters means that they are dimensionless. As a unit of time $(Kn_{1e}z_1(0))^{-1}$ is chosen while as the characteristic formation rate K, the value of the free molecular flux per unit of the cluster surface area is used. All the other notations are determined by the relations

$$R(f_j)=(a_jf_j-c_j)(f_j-1),$$

$$a_j=[\overline{K_{j+2}^+}(1-\delta_{j,N-1})-\overline{K_{j+1}^+}]S_0,$$

$$c_j=[\overline{K_{j+1}^-}-K_j^-(1-\delta_{j,r+1})]/(n_{1e}z_1(0)),$$

$$\mu_j=\frac{\overline{K_j^-}}{n_{1e}z_1(0)}\left(1-\frac{f_j}{f_{j-1}}\right)(1-\delta_{j,r+1})$$
$$-\overline{K_{j+2}^+}S_0f_j^2\left(1-\frac{f_{j+1}}{f_j}\right)(1-\delta_{j,N-1}), \tag{8}$$

and δ_{ij} is the Kronecker delta.

As shown in Refs. 26 and 11 at condensation under the adiabatic conditions (flows in nozzles, jets, thermal diffusion chambers) f_j is in fact, a smooth function of j therefore $\mu_j \ll 1$. If one neglects these terms in Eq. (7) then the equations of the examined system at $j>r+1$ break into the independent ones.

Further we may take advantage of the analysis[26,12] which shows that in the case of quasiequilibrium distribution of monomers over the internal degrees of freedom among all new variables the slow ones are only S and f_j, $j>\overline{j}\equiv(2/3\epsilon)^3$, $\epsilon\ll 1$ while all the others f_j are fast. Therefore in Eq. (7) the RHS of the equation for S is of the order of ϵ.

In our case the distribution of monomers over the rotational degrees of freedom is affected by collisions with the other monomers and radiative processes. As is known rotationally excited molecules relax practically over one collision. It means that $C_c/Kn_{1e}z_1(0)=O(1)$ therefore the rate of relaxation is at least not less than the rate of condensation. Thus the equation for S_0 can be rewritten in the form

$$\frac{dS_0}{d\tau}=-\frac{1}{K(n_{1e}z_1(0))^2}\sum_{k=1}^{M}(\Omega_k^c+\Omega_k^r). \tag{9}$$

As $C_c/Kn_{1e}z_1(0)=O(1)$, in Eq. (7) the RHS of the equations for dimensionless $x_1(k)$ are of the order of $O(1)$. Therefore these variables are fast. Thus we can omit the term dS_0/dr presented in the RHS of Eq. (7) for all f_j. It is reasonable because it is only an abbreviation for dimensionless $\Omega_k^c+\Omega_k^r$ and if $x_1(k)$ is a fast variable then $\Omega_k^c+\Omega_k^r=0$. Further applying once again the method of ''boundary functions'' to solve a full system Eq. (7) we again instead of differential equations for the fast variables f_j and $x_1(k)$, $k=0,\ldots,M-1$ get the following system of algebraic equations.

$$
\begin{aligned}
&0=Y_j, \quad j=1,\ldots,r,\\
&0=R_j+\delta_{j,r+1}\frac{n_{re}}{n_{r+1,e}S_0}\frac{f_{r+1}}{f_r}\frac{\overline{\gamma}}{Kn_{1e}z_1(0)}\hat{I}_u,\\
&\qquad j=r+1,\ldots,\overline{j},\\
&0=\Omega_k^c+\Omega_k^r, \quad k=0,\ldots,M-1.
\end{aligned} \tag{10}
$$

It is seen that the equations of the second line of this system at $j>r+1$ are independent and their solution can be easily obtained in an explicit form. Between two existing roots one has to choose the smallest one because only this root is stable. Equations of the first line can also be solved explicitly which results in analytic expressions of all f_j, $j=1,\ldots,r$ through S_0 and f_{r+1}. These analytic solutions should then be substituted in the equations for S, S_0, $x_1(k)$, $k=1,\ldots,M-1$ and slow f_j with j high enough (the typical numbers of slow f_j correspond to $j>10^5$). It can be shown that the contribution of slow f_j to the variation of S is small as compared with fast f_j and can be neglected. Thus the equation for S becomes independent on these slow f_j and can be solved together with the algebraic equations, Eq. (10). All the other n_j, $j>1$ [and consequently $x_j(k)$] one may calculate using already found S_0 and T according to the respective analytical formulas.

Such a program has been completely realized in Refs. 26 and 12 in the case of fast relaxation of monomers, i.e., when $x_1(k)=s_1(k)n_1z_1(k)$, $k=0,\ldots,M_1$. The quasisteady solutions obtained have the form

$$
\begin{aligned}
&f_j=1, \quad j=1,\ldots,x, \quad x=1+\max(r,j_*),\\
&f_j\cong\frac{1}{S}\left(1-\frac{b}{3j^{1/3}}\right)\exp\left(\frac{2b}{3j^{1/3}}\right), \quad j=x+1,\ldots,\overline{j},
\end{aligned} \tag{11}
$$

where b is the dimensionless surface energy of the cluster per its surface and j_* is determined by the chosen values of the formation and decay rate constants and is close to the critical size.[26,12]

In our case equations for f_j, $j>r+1$ have the same solutions as Eq. (11) if we change S for S_0. Note that the full equations for f_j, $j>r+1$ arisen from Eq. (7), if we omit in them terms μ_j, also have analytical solutions because these equations are the familiar Riccati ones with a known partial solution $f_j=1$.[26,12] Under such a condition the Riccati equation has an integral[29]

$$
\begin{aligned}
&f_j=\frac{C+\int(a_j+c_j)E\,dx-E}{C+\int(a_j+c_j)E\,dx+E},\\
&E=\exp\int(a_j-c_j)dx, \quad C=\frac{1+f_{j0}}{1-f_{j0}},
\end{aligned} \tag{12}
$$

where f_{j0} is the initial value of f_j at the moment $t=0$.

In order to solve the remaining equations it is necessary to exclude the term $\hat{I}_u$ from the equation $Y_r=0$ and the equation for f_{r+1}, substituting in them the equality $Y_{r-1}=0$ that gives rise to the closed equations for f_{r+1}

$$
(f_{r+1}-1)[\overline{K_{r+3}^{+}}S_0f_{r+1}-\overline{K_{r+2}^{-}}]=0. \tag{13}
$$

This equation has two roots

$$
\begin{aligned}
&f_{r+1}=1,\\
&f_{r+1}\approx\frac{1}{S_0}\exp\left[\frac{2}{3(r+1)^{1/3}}\right].
\end{aligned}
$$

It is easy to show that they coincide at $j_*\approx r+1$. Further two different situations can be considered.

1. Case $x>r+1$

In this case the stable root of Eq. (13) is $f_{r+1}=1$. Therefore the solution of all the other equations for f_j, $j=1,\ldots,r$ can be found from the condition $Y_j=0$, $\hat{I}_u=0$. Omitting an intermediate algebra we get

$$
\begin{aligned}
&f_j=1, \quad j=1,\ldots,r-2,\\
&f_{r-1}=(qS_0+1)\frac{1+qa(1-S_0)}{q+1+qa(1-S_0)},\\
&f_r=\frac{1}{1+qa(1-S_0)},
\end{aligned} \tag{14}
$$

where

$$
\begin{aligned}
&q=\tau_rC_{rMM}n_{1e}z_1(0),\\
&p=\theta\tau_r\left(1-\frac{\mathscr{E}_{r,MM}}{\nu\theta}\right)=1+qS_0,\\
&a=-\frac{1}{1+[(\nu\theta-\mathscr{E}_{rMM})(\tau_r\theta+\psi)/(2\mathscr{E}_{rMM}-\nu\theta)]},\\
&\psi=\sum_{k=1}^{M-1}\frac{z_r(k)}{z_r(M)}\frac{\mathscr{C}_{r,kM}\overline{x_1}(0)}{\mathscr{C}_{r,kM}\overline{x_1}(0)+\tau_r^{-1}}.
\end{aligned} \tag{15}
$$

It can be shown that f_{r-1} and f_r are positive at $S_0>0$. At $S_0=1$ one gets from Eq. (14) $f_{r-1}=f_r=1$.

Note that the obtained solutions of Eqs. (11) and (14) obey the condition of ‘‘smoothness’’ for all f_j at $j\geqslant r+1$.

As the result of all the transformations performed the rest system of kinetic equations takes the form

$$
\begin{aligned}
\frac{1}{z_1(0)}\frac{dS}{d\tau}=&-\sum_{j=x+2}^{N-1}[1+(r+1)\delta_{j,r+2}]\overline{K_j^{+}}\beta_{j-1}S_0^j\\
&\times\frac{1+qS_0}{1+q+qa(1-S_0)}(1-f_{j-1})\prod_{i=x+1}^{j-1}f_i,\\
&0=\Omega_k^c+\Omega_k^r, \quad k=0,\ldots,M-1.
\end{aligned} \tag{16}
$$

The leading term in the second sum in the equation for S is the first one which corresponds to $j=x+2$. Then neglecting the rest of the terms (see details in Refs. 26 and 12) we finally find

$$
\begin{aligned}
&\frac{1}{z_1(0)}\frac{dS}{d\tau}=-[1+(r+1)\delta_{x,r+2}]\beta_{x+1,e}\\
&\qquad\times S^{x+1}\overline{K_{x+1}^{-}}\frac{b}{6x^{4/3}}\frac{1+qS_0}{1+q+qa(1-S_0)},\\
&0=\Omega_k^c+\Omega_k^r, \quad k=0,\ldots,M-1.
\end{aligned} \tag{17}
$$

All the other steady-state concentrations except that for very large clusters with $j \gg 10^6$ could be found based upon the inverse transformation from variables f_j to variables n_j.

2. Case $x = r + 1$

Here $j_* < r+1$ therefore the stable root of Eq. (13) is $f_{r+1} \approx (1/S_0) \exp[2/3(r+1)^{1/3}]$. Then $\hat{I}_u$ does not vanish now but from the condition $Y_r = 0$ could be expressed through f_r

$$\hat{I}_u = -\alpha f_r,$$

$$\alpha = \frac{K^{+}_{r+2} n_{1e} z_1(0)}{\bar{\gamma}} S_0^2 \frac{n_{r+1,e}}{n_{re}} \left\{ 1 - \frac{1}{S_0} \exp\left[\frac{2}{3(r+1)^{1/3}} \right] \right\}. \tag{18}$$

Now from the equations $Y_j = 0$, $j = 1,...,r-2$ we find the values of f_j

$$f_j = 1 - \frac{\phi_j \alpha}{S_0 \tau_r \theta \tau_r} f_r f_{r-1}. \tag{19}$$

Quasisteady equations $Y_{r-1} = Y_r = 0$ can be solved in a similar way as in case 1. It yields

$$f_{r-1} = (qS_0 + 1) \frac{1 + \bar{\alpha} + qa(1-S_0)}{1 + q + \alpha + \bar{\alpha} + qa(1-S_0)},$$

$$f_r = \frac{1}{1 + \bar{\alpha} + qa(1-S_0)}, \tag{20}$$

where

$$\bar{\alpha} = \frac{\bar{\gamma}\alpha}{p\gamma_1 - \bar{\gamma}}.$$

It can be shown again that f_{r-1} and f_r are positive at least at $S_0 \geqslant 1$. However, now even at $S_0 = 1$ all f_j, $j = 1,...,r+1$ differ from unity.

Although f_{r+1} differs from unity the solution of Eq. (20) still obeys the condition of ‘‘smoothness’’ for f_j at $j \geqslant r+1$. Substituting these solutions into the equation for the slow variable S and keeping only the leading terms one finally gets

$$\frac{1}{z_1(0)} \frac{dS}{d\tau} = \beta_{r+2} S_0^{r+2} \bar{K}_{r+2} \frac{b}{6(r+1)^{1/3}} \times \frac{1 + qS_0}{1 + \alpha + \bar{\alpha} + q + qa(1-S_0)}. \tag{21}$$

Analysis of Eq. (19) shows that f_j, $j = 1,...,r-2$ become negative for $j < b/\ln S_0$. However, at S_0 which obeys the condition

$$\ln S_0 > \frac{b}{(r+1)^{1/3}}$$

the RHS of Eq. (21) becomes of the order of $O(1)$ or in the other words S becomes a slow variable. Since this S_0 we can no longer use the quasisteady equations for f_j because the specific rate of evolution of all f_j and S_0 is close to each other [the RHS of Eq. (21) is of the same order as the term $\Omega_0^c + \Omega_0^r$ in Eq. (7), therefore $\Omega_0^c + \Omega_0^r$ does not vanish]. Thus in this case it is necessary to solve the full system of coupled differential equations, Eq. (7), and further simplifications are impossible by virtue of the absence of small parameters in the system.

IV. DISCUSSION

The proposed theory of nucleation in the presence of radiation exciting the rotational degrees of freedom of the condensible molecules and methods of the asymptotic integration being applied to the studied problem allow one (i) from the very beginning to formulate the original problem at the microscopic level and (ii) to avoid some physical assumptions which are inherent to usual macroscopic approaches. Finally, our approach results in a radical simplification of the kinetic equations and reduces them to the kinetic equations only for populations of the rotational levels of monomers. The other cluster concentrations with $j \geqslant 2$ and populations of the intracluster vibrational states are determined by the explicit analytical formulas through already known S and T.

A. Justification of the method

In order to verify the accuracy of the method in Ref. 22 an analytical solution of the usual quasichemical equations of nucleation for a finite system with N molecules

$$\begin{aligned} dn_1/dt &= -\sum_{j=3}^{N} I_j - 2I_2, \\ dn_j/dt &= I_j - I_{j+1}, \quad j = 2,N-1, \\ dn_N/dt &= I_N, \end{aligned} \tag{22}$$

obtained with the help of our approach was compared with the numerical solution of these equations. Two important facts were taken into account. First, since we compare the analytical and numerical solutions without analyzing their physical meaning, we can compare them at model values of the rate constants presented in the original equations. It is necessary only that these model rate constants satisfy the assumptions made for the real condensing system. Second, as follows from the explicit form of the equilibrium function n_{je} (see below) and some estimations, the assumption of MCT made that $n_{je}/n_{1e} \ll 1$ at $j \geqslant 2$ and justified for an infinite system is invalid for small N (the choice of N is limited by the computer capacity). Therefore in test calculations we did not consider Eq. (22) but a net of equations normalized in another way, namely:

$$\begin{aligned} dn_1/dt &= -\sum_{j=3}^{N} I_j (d_{j+1} - d_j) - d_2 I_2, \\ dn_j/dt &= I_j - I_{j+1}, \quad j = 2,N-1, \\ dn_N/dt &= I_N, \quad d_j = \exp(j^{-l}), \\ n_1 &+ \sum_{j=2}^{N} d_j n_j = n. \end{aligned} \tag{23}$$

It can easily be shown[22] that an analytical solution to these equations is constructed exactly as described in the previous section and that at $l = 5-10$ the mentioned assump-

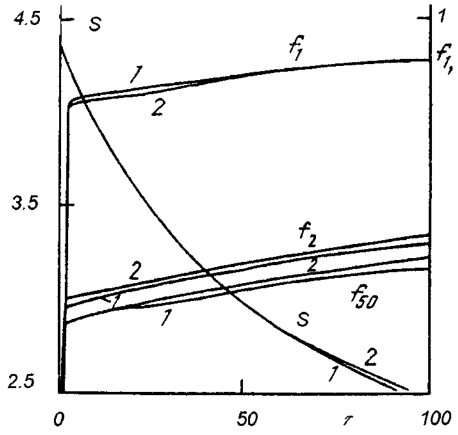

FIG. 1. Dependences of S, f_1, f_2, and f_{50} as functions of the dimensionless time τ obtained in the test example: 1, our analytical solution; 2, numerical solution, $N=100$.

tions are valid at $N\approx 100$. Figure 1 shows the results of this test. Details of the numerical procedure in use are described in Ref. 22. Calculations were performed with $N=100$, 1000, and 10 000. It is seen that our analytical method predicts the numerical results with the accuracy of the first approximation (for this test $\epsilon<0.01$). After a short initial period functions f_j reach their quasisteady values and during their further evolution they depend on time implicitly only due to their dependence on $S=S(t)$. A good agreement of the data confirms that the suggested approach is very promising.

B. Parameters and constants of the theory

For potential users of the theory further we also briefly present explicit expressions for the rate constant of the cluster formation and decay but a more detailed theory can be found in Ref. 12.

1. Rate constant K_j^+

In the case of an equilibrium distribution of the internal energy of a cluster the rate of the cluster formation K_j^+ could be expressed through the rate of the cluster unimolecular decay K_j^- using the relationship of the detailed balance

$$K_j^+=K_j^- n_{j+1,e}/n_{je}n_{1e}. \tag{24}$$

For K_j^- the explicit representation has been found in[23,24]

$$K_j^-\approx W_d(T)j^{2/3}\exp(-E_a/k_BT). \tag{25}$$

Here

$$W_d(T)=\frac{8h\nu_l}{k_BT}Z_{1,2,r}^+\left(\frac{\eta}{d_1}\right)^2\nu_t(1+1/\alpha_t),$$
$$\alpha_i=\exp\left(\frac{h\nu_i}{k_BT}\right)-1,\quad i=t,l,\quad \eta=(3m_1/4\pi\rho_l)^{1/3}. \tag{26}$$

ν_t and ν_l are translational and librational intermolecular vibrations in the cluster, considering in a harmonic approximation, m_1 is the molecular mass, ρ_l is the liquid density, and h and k_B are the Planck and Boltzmann constants. The definition of $Z_{1,2,r}^+$ is given further in the paragraph devoted to n_{je} and $P_{1,0}$ is given by the expression

$$P_{1,0}=\sqrt{\frac{2\pi}{3}}\left(\frac{\epsilon'}{k_BT}\right)^{1/6}\exp\left[-\frac{3}{2}\left(\frac{\epsilon'}{k_BT}\right)^{1/3}+\left(\frac{\epsilon_{LD}}{k_BT}\right)\right], \tag{27}$$

where

$$\epsilon'=m_1(\nu_t/a)^2. \tag{28}$$

Here $a=1/\sigma_{\mathrm{LD}}$ and σ_{LD} and ϵ_{LD} are parameters of the Lennard–Jones potential. For the activation energy we use an approximation

$$E_a=E_b\left(l_1-\frac{l_2m}{(j+m-2)}\right), \tag{29}$$

where E_b is the average dissociation energy per bond, and the term in parentheses is the average number of bonds of a molecule which could be capable of leaving the cluster with the other molecules in the cluster. Constants E_b, ν_t, l_2, l_1, $d_1\approx 2\sigma_{\mathrm{LD}}$, m_1 for some substances are given in Ref. 12.

2. Function n_{je}

An explicit form of this function depends upon the physical model of the cluster. Nevertheless, the common expression of[22]

$$n_{je}=\overline{A_j}(T)\exp(-bj^{2/3}) \tag{30}$$

should be valid for any model and the matter is to specify A_j which weakly depend upon j. For instance, for a simple model of the cluster which has been previously used by Ref. 30 it is possible to get

$$\overline{A_j}=\lambda_1^{-3}j^{3/2}Z_{jR}\theta^6\exp[l_1\epsilon_0(2)/k_BT]\exp(3\theta), \tag{31}$$

where λ_j is the de Broglie thermal wavelength

$$Z_{jR}=\frac{8\pi^2}{h^3\chi_j}(2\pi k_BTJ_j)^{3/2},\quad J_j=\frac{2}{5}m_1jR_j^2,\quad R_j=\eta j^{1/3}, \tag{32}$$

χ_j is the number of the axes of symmetry of the j cluster, $\epsilon_0(2)<0$ is the dimer potential well, $\theta=h\nu_{3t}/k_BT$. The minimum frequency of the intracluster translational oscillations ν_{3t} for some substances is given in Ref. 12.

As far as n_{1e} is concerned the analysis of Ref. 22 shows that it could be determined with the help of the well-known Clapeyron–Clausius relationship.[31]

As shown in Ref. 12 when utilizing these constants MCT predicts the available experimental data on nucleation in streams and permits one to explain many experimentally observed phenomenon.

C. Main assumptions and problems of the theory

Note that all assumptions made at the asymptotic integration of the initial system are discussed in detail in Ref. 12 therefore we omit this discussion here. In addition, we have already discussed above the existing theoretical background which provides evidence to assume that only the water molecules being in a ground rotational para state are efficient to be attached to the cluster while the probability to form molecular complexes from the water molecules being in the other rotational states is negligible.

Nevertheless we would like to highlight the main problems of MCT left to be solved in the future. First it is reasonable to note that from the mathematical point of view there is no sharp boundary between the fast and slow variables as well as between the areas where the limit of ''high and low pressures'' have been introduced. Under such conditions our idea of the parameter r could be very attractive for physicists but not for mathematicians because we have no evidence for introducing such a sharp transition. This problem has already been discussed in Ref. 12 where, however, a weak influence of this simplification on the value of supersaturation and the integral parameters of the system has been revealed. As far as the cluster concentrations are concerned, a more precise definition of this boundary apparently should greatly affect the value of concentrations for clusters with j about r, but for other clusters such concentrations should be close to those obtained here.

A similar situation arises when calculating the precise values of the cluster concentrations by means of the f variables which have been found as a solution of our quasisteady equations. The problem is that according to the f definition in Eq. (6) a reverse transformation from f to n concentrations leads to considerable errors at large values of j. The matter is that small errors in calculating f, inherent to any asymptotical method, are summed with one another giving rise to the large errors in n_j.

At the same time our results of numerical calculations of various condensible gas flows in smooth nozzles, jets, and nozzles with a contour fracture demonstrate the capability of MCT to predict the experimental data in a wide range of temperatures and pressures with only the parameter l_1 for fitting, which is the average number of bonds per molecule in a large cluster.[23,12] Moreover, this parameter has a clear physical sense and, in principle, could be obtained from quantum chemistry.

In any case one could consider MCT as a more consistent way to adopt some ideas of the kinetic theory of chemical reacting gases and an asymptotical analysis as applied to the nucleation problem.

D. Behavior of the system in the vicinity of $x=r+1$

Let us further give a brief analysis of the solution obtained. First, by means of some transformations we would come to a more evident form of the solution for the product $f_r f_{r-1}$, namely:

$$f_r f_{r-1} = 1 + \frac{q(S_0-1)(1+a)}{1+q+qa(1-S_0)}, \quad x>r+1,$$

$$f_r f_{r-1} = 1 + \frac{q(S_0-1)(1+a)-d}{1+q+qa(1-S_0)+d}, \quad x=r+1,$$

$$a = \frac{1+qS_0-\mathcal{E}_{rMM}\tau_r\nu^{-1}}{\mathcal{E}_{rMM}\tau_r\nu^{-1}+(1+qS_0)(\mathcal{E}_{rMM}\tau_r\nu^{-1}+qS_0+\psi)} \tag{33}$$

$$d \equiv \alpha + \overline{\alpha}$$

$$= \alpha \frac{qS_0(1+\mathcal{E}_{rMM}\tau_r\nu^{-1}+qS_0+\psi)+\psi}{qS_0(1+\mathcal{E}_{rMM}\tau_r\nu^{-1}+qS_0+\psi)+\mathcal{E}_{rMM}\tau_r\nu^{-1}+\psi}.$$

It is seen that $0<a<1$ because $\mathcal{E}_{rMM}\tau_r\nu^{-1}<1$ and $q \sim 1$ and $d>0$. In view of this $f_r f_{r-1}>1$ at $x>r+1$ and $f_r f_{r-1}<1$ at $x=r+1$. As dS/dt is proportional to $f_r f_{r-1}$, when x crosses the point $r+1$ the character of the dependence dS/dt on S_0 changes a little. However, as far as f_j, $j=1,...,r-2$ is concerned at $x=r+1$ the further increase of S_0 results in the decrease of these f_j. In order to prove this statement let us give a more explicit expression for the product $\phi_j \alpha / S_0 \tau_r \theta \tau_r$, which is presented in Eq. (19). In doing so note that from the α_j definition given in Eq. (A15) we have

$$\alpha_3 \mathcal{E}_{3MM} = 1 + S_0 \frac{n_{2e}C_{2MM}z_2(M)}{n_{1e}C_{100}z_1(0)},$$

$$\alpha_4 \mathcal{E}_{4MM} = 1 + S_0 \frac{n_{3e}C_{2MM}z_2(M)}{n_{2e}C_{100}z_1(0)} \times \left(1 + S_0 \frac{n_{2e}C_{2MM}z_2(M)}{n_{1e}C_{100}z_1(0)}\right),$$

etc. Leaving in these expressions only the leading term one gets

$$\alpha_{j+2}\mathcal{E}_{j+2,MM} = \frac{n_{j+1,e}C_{j-1,MM}z_{j+1}(M)}{n_{1e}C_{100}z_1(0)} S_0^j.$$

Let us assume that K_j^+ is proportional to $j^{2/3}$ as it is usually done. Thus we can finally represent Eq. (19) in the following approximate form

$$f_j = 1 - f_r f_{r-1} \frac{(r+2)^{2/3}}{S_0^2} \beta_{r+1} S_0^{r+1}. \tag{34}$$

It turns out that within this representation the RHS of Eq. (34) does not depend on j. Certainly this dependence will arise if we take into account the omitted terms. It is seen that since $\ln S_0 > b/(r+1)^{1/3}$ the coefficient at $f_r f_{r-1}$ becomes of the order of unity that results in the decrease of f_j. We remind the reader that at the same S_0 the RHS of Eq. (21) becomes also of the order of unity and S becomes a slow variable (see the previous section).

E. Influence of radiation

Here we discuss the influence of radiation on the condensation kinetics analyzing Eq. (17). First we consider a weak comet with a small production rate of water vapor from the cometary nucleus. It means that the numerical density of the vapor is small enough that it results in a low value of the relaxation rate C_c. Under these conditions the radiative processes dominate the collisional relaxation ($\Omega_k^c \ll \Omega_k^r$), and the steady distribution of populations is mostly determined by the external radiation, i.e., by the interaction of water molecules with the radiative flux from the sun. As a result the populations of the rotational levels of monomer are nonequilibrium. They can be expressed through n_1 or S by solving the system which follows from Eq. (17)

$$\Omega_k^r = 0, \quad k=0,...,M-1, \qquad x_1(M) \equiv n_1 - \sum_{k=0}^{M-1} x_1(k). \tag{35}$$

Then substituting these solutions into the first equation of Eq. (17) we get the closed equation for S, where S_0 depends upon S in a certain way and, in principle, this dependence may have a rather unusual and complex form.

Another situation takes place for active comets with a high production rate. Here the increase of the initial vapor density results in more frequent collisions, which reduce the rate of the collisional relaxation C_c so that it becomes more than the rate of the radiative processes $(\Omega_k^c \gg \Omega_k^r)$. As a result, the equilibrium distribution of the energy of rotational sublevels is established, i.e., $\overline{x_1}(k) = n_1 z_1(k)$. Hence $S = S_0$ and the equation for S in Eq. (17) becomes closed. The difference with the previous situation is that the RHS of the equation for S in the last case depends on S rather than in the first case (generally speaking, more simply).

At the intermediate distances both terms Ω_k^c and Ω_k^r could be of the same order of magnitude therefore quasisteady populations $x_1(k)$, $k = 0,...,M$ are nonequilibrium and should be found by solving the full system Eq. (17). Note that the correlation between Ω_k^c and Ω_k^r can vary from one rotational sublevel to another in accordance with the value of the Einstein coefficients.

The gas production rate of the comet increases as the distance between the comet and the sun decreases. On the other hand the decrease of this distance also results in the increase of the radiation intensity (see Ref. 1) therefore these two processes are competitive. For concrete estimations simulation is needed.

F. Comparison with the classical nucleation theory

It is feasible to compare MCT with the classical nucleation theory. Such a comparison is completely given in Ref. 12 for the case of homogeneous nucleation (no radiation) and here we emphasize only one point. In the classical nucleation theory a special role is ascribed to the critical nucleus which is determined as a droplet being in equilibrium with the surrounded supersaturated vapor. It is assumed that drops with $j > j_*$ are capable of further growth while drops with $j < j_*$ tend to decrease their size. Accordingly, the rate of nucleation is determined as the number of critical nuclei formed per unit of time and volume.

In contrast the analysis of our results brings an unusual conclusion that all clusters with size $j < x$ are in quasiequilibrium, i.e., for all those clusters $n_j = n_{je} S^j$, where $n_{je} \approx A(T)\exp(-bj^{2/3})$ is an equilibrium cluster concentration and b is the dimensionless surface energy per one surface molecule.[22] Thus for these clusters all fluxes $I_j = K_j^+ n_{j-1} n_1 - K_j^- n_j$ vanish (i.e., $n_j = \text{const}$) while within the classical theory $I_j = I = \text{const}$ and this value is usually accepted as the nucleation rate. Hence if $x \approx j_*$ our result still correlates in a certain way with the prediction of the classical theory. However, if $j_* < x = r+1$ than within our theory all clusters with $j < r+1$ are in quasiequilibrium while within the classical theory it is not the case. In particular, it is known from the literature that for condensation of water vapor in the air at low temperatures $T < 270$ K (such low temperatures are also inherent to the cometary conditions) the size of the critical nucleus determined by the classical theory turns out to be less than the water molecule itself that shows the internal contradictions of the theory. However, these contradictions are not inherent to MCT because (i) MCT does not use the concept of a certain special droplet like the critical nucleus and (ii) even if we account for the classical concept of the droplet being in the equilibrium with the surrounded vapor, at $x = r+1$ this is not the critical nucleus in our theory but all clusters with $j \leqslant r+1$. Moreover, our direct calculations of the condensible flow of the pure water vapor and the moist air show that MCT predicts rather well the experimentally observed dependences. The results are discussed in detail in Refs. 32 and 12.

This statement is valid even for homogeneous condensation of pure vapor without radiation. In the case of radiation affecting the condensation kinetics, this influence becomes apparent to (i) the form of the cluster distribution function; (ii) the form of the dependence of S upon t; (iii) the dependence of S upon I at the intermediate gas production rates when $\Omega_k^c \sim \Omega_k^r$.

In conclusion we note that the method proposed being generalized for spatially nonuniform systems, flows of the condensible vapor, gives an opportunity to simulate condensation in the inner coma with allowance for the influence of the external radiation on the condensation kinetics. Indeed, it allows one to solve hydrodynamic equations in conjunction with the differential equation for supersaturation S and a finite system of algebraic equations for populations $x_1(k)$, $k = 0,...,M-1$ while the original system contains the infinite number of equations and one should cut it in a certain way in order to solve it numerically. The other cluster concentrations and populations of their energetic levels are analytically expressed through S_0 and T. The results of such a simulation and a convenient and economic algorithm which combines analytical and numerical approaches and gives the possibility to restore the cluster size distribution function will be given elsewhere.

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APPENDIX A: QUASISTEADY SOLUTIONS FOR POPULATIONS

In this Appendix we determine quasisteady populations $x_j(k)$ which are the asymptotic solutions of Eq. (1). As it is not so simple to solve Eq. (1) at $j \leqslant r$, to make further progress in such a case we introduce a conception of the dissociation from the topmost level. The physical meaning of this parameter could be understood if we consider the dissociation process simulating the cluster by a large molecule with harmonic intracluster oscillations. There is an infinite number of energetic vibrational levels in such a system in contrast to the real anharmonic oscillators for which the number of levels is limited by the dissociation threshold. In order to take this effect into account we need to cut off those levels which are unimportant from the physical point of view.

In virtue of the r-parameter definition the following remark is in order that, in principle, in the j cluster for each level k the own relationship between the dissociation $E_j(k)$ and relaxation $R_j(k)n_1$ rates at this level could exist. Moreover, it can be shown that the ratio $E_j(k)/R_j(k)n_1$ at given j increases with k growth so that at high k the dissociation rate is always higher than the relaxation one for arbitrary j. Therefore it may seem that the concept of the number r in MCT is a failure. However, fortunately these top levels do not bring any essential contribution to the fluxes I_j presented in the RHS of Eq. (1). Indeed, substituting the quasisteady solution obtained at $j>r$ in Eq. (2) with allowance for the flux I_j definition given in Eq. (2) one gets

$$I_j=K_j^+ n_{j-1}\overline{x_1}(0)-K_j^- n_j\,,$$

$$K_j^-=\sum_{k,l} E_j(k|0,l)z_j(k), \qquad \text{(A1)}$$

$$K_j^+=K_jK_j^-=\sum_{k,l} C_{j-1}(l,0|k)z_{j-1}(k).$$

Rate constants $E_j(k|0,l)$ are proportional to $s_j(k)$, the degree of degeneracy (the statistical weight) of level k. For the system of s identical oscillators contained k quanta $s_j(k)$ could be determined by the expression $s_j(k)=C_k^{k+s-1}=(k+s-1)!/k!s!$. On this account the function $s_j(k)z_j(k)$ may be considered as a δ function with a maximum in the point $k=M$ which holds the relationship $d[s_j(k)z_j(k)]/dk|_{k=M}=0$. Thus the considerable contribution in K_j^- bring only those levels which are close to M and more distant levels could be omitted from Eq. (1) due to their negligible contribution.

In accordance with this model Eq. (1) can be rewritten in a general form[12]

$$0=\sum_i\left[-I_j(k,i|M)+\delta_{kM}\sum_l I_{j-1}(l,i|M)\right],$$

$$j=2,...,r-1,$$

$$0=\sum_i\left[\delta_{kM}\sum_l I_{r-1}(l,i|M)-I_r(k,i|M)\right.$$
$$\left.+\sum_{l,\nu} J_r(l,i|k,\nu)\right],$$

$$0=\sum_{l,i,\nu} J_j(l,i|k,\nu), \quad j=r+1,...,N,$$

where k varies from 1 to M. However, in our case in accordance with the already made assumption that only molecules being in a ground para state are able to attach the cluster this system should be transformed to the following final form

$$0=-I_j(k,0|M)+\delta_{kM}\sum_l I_{j-1}(l,0|M), \quad j=2,...,r-1,$$

$$0=\delta_{kM}\sum_l I_{r-1}(l,0|M)-I_r(k,0|M)+\sum_{l,i,\nu} J_r(l,i|k,\nu), \quad \text{(A2)}$$

$$0=\sum_{l,i,\nu} J_j(l,i|k,\nu), \quad j=r+1,...,N,$$

1. High-pressure limit $(j=r+1,...,N)$

In accordance with the parameter r conception in the high-pressure limit only the relaxation terms $\Sigma J_j(M,k|l,i)$ have to be kept in Eq. (A2). Thus independently upon the explicit form of these terms the following solution

$$\overline{x_j}(k)=n_j z(k)\omega_{jk}(\overline{x_1}(1),\dots,\overline{x_1}(M),\overline{n_1},T) \qquad \text{(A3)}$$

completely satisfies the reduced equations. More obvious representation of Eq. (A2) can be obtained at least for two models of the relaxation term, the model of the single-quantum transitions and the BGK model. In the second case it is managed to reach a radical simplification of the final expressions so that they can be written in the explicit form for an arbitrary distribution of the monomer populations. The BGK model (the model of "strong" collisions) assumes that during the specific time τ_j the population of any lth level $x_j(l)$ is able to relax to its equilibrium value that yields $\omega_{jk}\equiv 1$. Just the same solution can be obtained if the rate of the monomer relaxation greatly exceeds the dimer dissociation rate ("fast relaxation") or for monoatomic vapor condensation.

2. Low-pressure limit $(j=2,...,r-1)$

In this section we consider a method which allows one to solve asymptotically the quasisteady equations (A2) in the low-pressure limit. In such a case two situations should be discussed, namely: (i) the dissociation rate from the top-most level $E_j(M|0,k)$ decreases faster than the rate of relaxation $\Sigma i,\nu R_j(k,\nu|k-1,i)$ with k drop; (ii) for all k one has $E_j(M|0,k)>\Sigma_{i,\nu}R_j(k,\nu|k-1,i)$. From the physical consideration the first case is more real and we shall discuss further just this one. The second situation is studied in Ref. 18 giving rise to the similar results.

Figure 2 illustrates the situation under consideration. Here along the abscissa axis the number of the cluster vibrational level is set down, j is the cluster size, $f_{d,j}(k)=E_j(M|0,k)z_j(M)$, $f_{R,j}(k)=\Sigma_{i,m}R_j(k,i|k-1,m)n_{1e}z_1(i)z_j(k)$. The low-pressure limit is considered and therefore for the topmost level M_j the following relationship is valid

$$f_{d,j}(M)\gg f_{R,j}(M)>\sum_{i,m} R_j(M,m|l,i)n_{1e}z_1(m)z_j(M),$$

$$l=0,...,M-2.$$

The last condition is rather obvious because the rate of single-quantum transitions from a certain level is much more than the rate of multiquantum transitions from the same level.

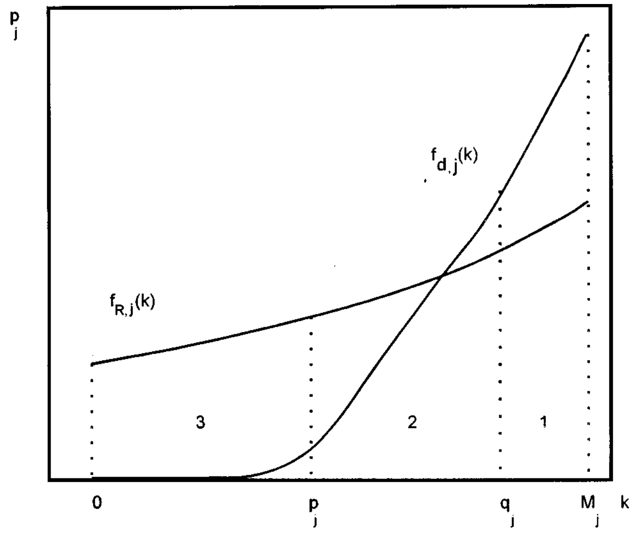

FIG. 2. The case where the cluster dissociation rate at the topmost level $E_j(M|0,k)$ decreases faster than the rate of relaxation $\Sigma_{i,m}R_j(k,m|k-1,i)$ with k drop.

We proposed that $f_{d,j}(k)$ decreases faster than $f_{R,j}(k)$ with k drop therefore starting from a certain level q_j dissociation and relaxation rates will be of the same order $[f_{d,j}(k)\sim f_{R,j}(k)]$. This situation takes place for numbers from q_j up to another certain level p_j. For less than p_j levels one has $f_{d,j}(k)/f_{R,j}(k)\ll 1$. Thus the numbers p_j and q_j split all the levels into three areas. In region $1(k=q_j+1,...,M_j)$ one has $f_{d,j}(k)/f_{R,j}(k)\gg 1$, that reduces the system Eq. (A2) to the form

$$\delta_{kM}\sum_{m=q_{j-1}+1}^{M-1} I_{j-1}(m,0|M)-I_j(k,0|M)=0,$$

$$k=q_j+1,...,M. \qquad \text{(A4)}$$

According to the assumption made the rate constant $E_j(M|0,k)$ decreases very fast with k drop therefore in Eq. (A4) we neglect all the fluxes $I_{j-1}(m,0|M), m=1,...,q_{j-1}$ as compared with $I_{j-1}(m,0|M)$, $m=q_{j-1}+1,...,M$.

In region 2 $f_{d,j}(k)\cong f_{R,j}(k)$ and from Eq. (A2) one gets

$$-I_j(k,0|M)+\sum_{m,l} J_j(l,i|k,m)=0, \quad k=p_j+1,...,q_j. \qquad \text{(A5)}$$

Finally in region 3 under the above assumptions the following equations are valid

$$\sum_{i,m,l} J_j(l,i|k,m)=0, \quad k\leqslant p_j. \qquad \text{(A6)}$$

Solving Eqs. (A4)–(A6) one can express all the populations $x_j(k)$, $j=2,...,r-1$, $k=1,...,M$ through n_j,n_1, $x_r(M),x_1(1),\dots,x_1(M)$. Below for each region we give a special method for solving the above presented equations.

a. Region 3 ($k\leqslant p_j$)

To further describe the relaxation processes for the sake of simplicity the BGK model with the relaxation time τ_j common for all levels of the j cluster is in use

$$\sum_{i,m,l} J_j(l,i|k,m)=-\frac{\overline{x_j}(k)-n_jz_j(k)}{\tau_j}. \qquad \text{(A7)}$$

This model brings quite an evident solution of Eq. (A6)

$$\overline{x_j}(k)=n_jz_j(k), \quad k=1,...,p_j. \qquad \text{(A8)}$$

b. Region 2 ($k=p_j+1,...,q_j$)

For $k=p_j+1,...,q_j$ from Eq. (A5) with allowance for the I_j and J_j definition given in Eq. (1) it is simple to get

$$\overline{x_j}(k)=\frac{\mathscr{E}_{j+1,Mk}\overline{x_{j+1}}(M)+n_jz_j(k)\tau_j^{-1}}{\mathscr{C}_{j,kM}\overline{x_1}(0)+\tau_j^{-1}},$$

$$k=p_j+1,...,q_j. \qquad \text{(A9)}$$

c. Region 1 ($k=q_j+1,...,M_j$)

As follows from Eqs. (A2) the quasisteady equations for populations in this region have the form

$$\begin{aligned} &I_j(k,0|M)=0, \quad k=q_j+1,...,M-1, \\ &\sum_l I_{j-1}(l,0|M)-I_j(M,0|M)=0, \quad j=2,...,r-1. \end{aligned} \qquad \text{(A10)}$$

We shall solve these equations on the base of the following reasoning. Our ultimate goal is to obtain the closed system of equations for concentrations. Each equation of this system has the form

$$\frac{dn_j}{dt}=\sum_{k,l} I_{j-1}(l,0|k)-\sum_{k,l} I_j(l,0|k),$$

and the above-mentioned model of dissociation from the topmost level being applied to this system yields

$$\begin{aligned} \frac{dn_j}{dt}&=\sum_l I_{j-1}(l,0|M)-\sum_k I_j(k,0|M) \\ &=\sum_l I_{j-1}(l,0|M)-I_j(M,0|M)-I_j(0,0|M) \\ &=-I_j(0,0|M). \end{aligned} \qquad \text{(A11)}$$

To get Eq. (A11) at first we used the first line of Eq. (A10) and then the last one accounting for the fact that at $k\leqslant q_j$ in the low-pressure limit one has $I_j(M,0|M)\gg\Sigma_i I_j(M,0|k)$.

In accordance with the above discussion about the dissociation rate constant behavior under the k change it is reasonable to assume that $\mu_j\equiv I_j(0,0|M)/I_j(M,0|M)\ll 1$. Hence in the first approximation over all μ_j we can rewrite Eq. (A11) as follows

$$\begin{aligned} &I_j(k,0|M)=0, \quad j=2,...,r-1, \quad k=q_j+1,...,M-1, \\ &I_1(0,0|M)-I_2(M,0|M)=0, \\ &I_{j-1}(M,0|M)-I_j(M,0|M)=0, \quad j=3,...,r-1. \end{aligned} \qquad \text{(A12)}$$

Having solved this system we may express all $x_j(k)$, $j=2,...,r-1$, $k=q_j+1,...,M$ through $x_r(M)$, $x_1(0),\dots,x_1(M)$, and $n_2,\dots,n_r$. Omitting an intermediate algebra we put down the final result

$$\overline{x_j}(M)=\frac{\xi_j+\alpha_j\mathscr{E}_{r,MM}\overline{x_r}(M)+(\xi_j\alpha_{r-1}-\alpha_j\xi_{r-1})\mathscr{C}_{r-1,MM}\overline{x_1}(0)}{1+\mathscr{C}_{r-1,MM}\overline{x_1}(0)\alpha_{r-1}},\quad j=2,...,r-1,$$

$$\overline{x_j}(k)=\overline{x_{j+1}}(M)\mathscr{E}_{j+1,Mk}/\mathscr{C}_{j,kM}\overline{x_1}(0),\qquad j=2,...,r-1,\quad k=q_j+1,...,M-1, \tag{A13}$$

$$x_j(0)=n_j-\sum_{k=1}^{M}x_j(k),$$

with the following notation introduced

$$\alpha_j=[1+\mathscr{C}_{j-1,MM}\overline{x_1}(0)\alpha_{j-1}]/\mathscr{E}_{j,MM},$$

$$\alpha_2=\left(\sum_{i,l}E_2(M|i,l)\right)^{-1}, \tag{A14}$$

$$\xi_j=n_{je}z_j(M)S_0^j, \tag{A15}$$

where $S_0=x_1(0)/n_{1e}z_1(0)$ is an analog of supersaturation. Note that the value of $x_r(M)$ in the above expressions is yet unknown and it is to be found from solving the corresponding equations in Eq. (A2) with $j=r$.

3. Intermediate case $j=r$

In accordance with the parameter r conception in such a case Eq. (A2) takes the form

$$\delta_{k,M}\sum_{l}I_{r-1}(l,0|M)-I_r(k,0|M)-\frac{\overline{x_r}(k)-n_rz_r(k)}{\tau_r}=0,\qquad k=1,...,M_r. \tag{A16}$$

Populations $x_{r+1}(k)$, $k=1,...,M$ have already been determined before Eq. (A1). Populations $x_{r-1}(l)$, $l=1,...,M$ which are presented in the equations for $x_r(M)$ also have been already obtained. Combining all these relationships within the framework of Eq. (A16) one can get

$$\overline{x_r}(k)=n_rz_r(k)\,\frac{C_r(k,0|M)\overline{x_1}(0)f_r+\tau_r^{-1}}{C_r(k,0|M)\overline{x_1}(0)+\tau_r^{-1}}$$

$$=-n_r(1-f_r)\,\frac{C_r(k,0|M)\overline{x_1}(0)}{C_r(k,0|M)\overline{x_1}(0)+\tau_r^{-1}}+n_rz_r(k). \tag{A17}$$

An expression for $x_r(M)$ directly follows from (A16) with allowance for the explicit representation of $x_{r-1}(M)$ given in Eq. (A13)

$$\overline{x_r}(M)=\frac{1}{\theta}\left[\frac{n_{re}z_r(M)}{\tau_r}+\frac{\mathscr{C}_{r-1,MM}\overline{x_1}(0)\xi_{r-1}}{\nu}+\mathscr{E}_{r+1,MM}n_{r+1}z_{r+1}(M)\right],$$

$$\nu=1+\mathscr{C}_{r-1,MM}\overline{x_1}(0)\alpha_{r-1},$$

$$\theta=C_r(M,0|M)\overline{x_1}(0)+\tau_r^{-1}+\mathscr{E}_{r,MM}\nu^{-1}. \tag{A18}$$

However, it would be convenient to represent this formula in another form. For this reason let us multiply $\overline{x_r}(M)$ by θ and subtract from this product term $n_{re}z_r(M)\overline{n}_{r+1}\theta/S_0$. It results in the following expression

$$\overline{x_r}(M)\theta-n_{re}z_r(M)\overline{n}_{r+1}\theta/S_0$$

$$=\frac{\mathscr{C}_{r-1,MM}\overline{x_1}(0)\xi_{r-1}}{\nu}-\frac{\mathscr{E}_{r,MM}n_{re}z_r(M)\overline{n}_{r+1}}{\nu S_0}+\frac{n_rz_r(M)}{\tau_r}-\frac{n_{re}z_r(M)\overline{n}_{r+1}}{S_0\tau_r}+\mathscr{E}_{r,MM}n_{r+1}z_{r+1}(M)-\frac{\mathscr{C}_{r,MM}\overline{x_1}(0)n_{re}z_r(M)\overline{n}_{r+1}}{S_0},$$

whence the representation for $\overline{x_r}(M)$ follows

$$\overline{x_r}(M)=n_rz_r(M)(1-f_r)\,\frac{1}{\theta\tau_r}-n_{re}z_r(M)\times\frac{\mathscr{E}_{rMM}}{\nu S_0\theta}\,(\overline{n}_{r+1}-S_0^{r+1})+n_{re}z_r(M)\overline{n}_{r+1}\times\frac{\theta+C_r(M,0|M)n_{1e}z_1(0)(1-S_0)}{\theta S_0}, \tag{A19}$$

$$f_r=\overline{n}_{r+1}/S_0\overline{n}_r. \tag{A20}$$

The convenience of Eq. (A20) is connected with the fact that in equilibrium $f_r=S_0=\overline{n}_{r+1}=1$, therefore the first and second terms in Eq. (A20) vanish. Thus we found all quasisteady populations $x_j(k)$.

APPENDIX B: QUASISTEADY EQUATIONS FOR CONCENTRATIONS

In this Appendix we give a brief deriving of quasisteady equations for concentrations which are based on the solution for the quasisteady populations given in Appendix A. Below we shall consequently get such equations in the high- and low-pressure limit as well as in the intermediate case $j=r$.

1. High-pressure limit ($j>r$)

In this region of j the quasisteady equations for concentrations follow from Eq. (A1) taking the common form

$$\frac{dn_j}{dt}=I_{j-1}-I_j(1-\delta_{jN}),\quad j>r, \tag{B1}$$

where the fluxes I_j have been introduced in Eq. (A1).

2. Intermediate case ($j=r$)

In order to derive the quasisteady equation for n_r we have to substitute the quasisteady values of populations in Eq. (A11). However, it is not directly feasible to do that because of a great complexity of the expressions appeared. On the other hand, in deriving the equations we are interested in, it is possible to use some relationships for the quasisteady populations which have already been used in Appendix A. Doing in such a way we obtain

$$\frac{dn_r}{dt}=\sum_l I_{r-1}(l,0|M)-\sum_k I_r(k,0|M)$$

$$=I_{r-1}(0,0|M)+I_{r-1}(M,0|M)+\sum_{l=1}^{M-1} I_{r-1}(l,0|M)$$

$$-I_r(0,0|M)-\sum_{k=1}^{M} I_r(k,0|M). \tag{B2}$$

We have intentionally divided the sums in Eq. (B2) into several parts in order to neglect some of them based on the evaluation of Appendix A. In particular, we can omit all the terms connected with condensation from the zero level that corresponds to the first approximation over the parameters μ_j (see Appendix A). Furthermore, in accordance with Eq. (A12) $\Sigma_{l=1}^{M-1} I_{r-1},(l,0|M)=0$. Finally, with allowance for Eq. (A16) one can rewrite Eq. (B2) as follows

$$\frac{dn_r}{dt}=\sum_{k=1}^{M} \frac{\overline{x_r}(k)-n_r z_r(k)}{\tau_r}. \tag{B3}$$

Now substituting $\overline{x_r}(M)$ from Eq. (A20) and $\overline{x_r}(k)$, $k=1,...,M-1$ from Eq. (A17) into Eq. (B3) one can get after some transformations

$$\frac{dn_r}{dt}=\frac{n_r(1-f_r)}{\tau_r}\left[\frac{z_r(M)(1-\tau_r\theta)}{\tau_r\theta}\right.$$

$$\left.-\sum_{k=1}^{M-1} \frac{C_r(k,0|M)\overline{x_1}(0)z_r(k)}{C_r(k,0|M)\overline{x_1}(0)+\tau_r^{-1}}\right]$$

$$-\frac{\mathcal{E}_{r,MM}n_{re}z_r(M)}{\nu S_0\theta\tau_r} I_{r+1}^{(2)}+\frac{n_r z_r(M) f_r}{\tau_r\theta}$$

$$\times C_r(M,0|M)n_{1e}z_1(0)(1-S_0), \tag{B4}$$

where $I_{r+1}^{(2)}=S_0^{r+1}-\overline{n}_{r+1}$.

3. Low-pressure limit (*j*<*r*)

First of all let us introduce a special notation $\hat{I}$ for the flux $I_{r-1}(M,0|M)$ which is important for further applications. By definition

$$\hat{I}=C_{r-1}(M,0|M)\overline{x_{r-1}}(M)\overline{x_1}(0)-E_r(M|0,M)\overline{x_r}(M),$$

With an eye to Eqs. (A20) and (A13) we can eventually express the flux $\hat{I}$ through the quasisteady concentrations that yield

$$\hat{I}=-\frac{\mathcal{E}_{r,MM}n_{re}z_r(M)}{\nu}\left\{\frac{\overline{n_r}(1-f_r)}{\tau_r\theta}+\frac{1}{S_0}\left(\frac{\mathcal{E}_{r,MM}}{\nu\theta}-1\right)\right.$$

$$\left.\times I_{r+1}^{(2)}+\frac{\mathcal{E}_{r,MM}n_{1e}z_1(0)}{S_0\theta}\overline{n}_{r+1}(1-S_0)\right\}. \tag{B5}$$

With the help of Eq. (B5) the quasisteady equations for n_j, $j<r$ can be found in a natural way. Indeed, in accordance with Eq. (A12)

$$\frac{dn_j}{dt}=-I_j(0,0|M)=\mathcal{E}_{j+1,M0}\overline{x}_{j+1}(M)$$

$$-\mathcal{C}_{j,0M}\overline{x_1}(0)\overline{x_j}(0),$$

whence with allowance for the $x_j(0)$ definition given in Eq. (1)

$$\frac{dn_j}{dt}=\mathcal{E}_{j+1,M0}\overline{x_{j+1}}(M)-\mathcal{C}_{j,0M}\overline{x_1}(0)\left[\frac{n_j}{s_j(0)}-\sum_{k=1}^{M-1}\overline{x_j}(k)\frac{s_j(k)}{s_j(0)}-\overline{x_j}(M)\frac{s_j(M)}{s_j(0)}\right]$$

$$=\mathcal{E}_{j+1,M0}\overline{x_{j+1}}(M)-\mathcal{C}_{j,0M}\overline{x_1}(0)\left[\frac{n_j}{s_j(0)}-\overline{x_{j+1}}(M)\sum_{k=1}^{M-1}\frac{s_j(k)}{s_j(0)}\frac{\mathcal{E}_{j+1,Mk}}{\mathcal{C}_{j,kM}\overline{x_1}(0)}-\overline{x_j}(M)\frac{s_j(M)}{s_j(0)}\right]$$

$$=-\mathcal{C}_{j,0M}\overline{x_1}(0)\left[\frac{n_j}{s_j(0)}-\overline{x_{j+1}}(M)\sum_{k=0}^{M-1}\frac{s_j(k)}{s_j(0)}\frac{\mathcal{E}_{j+1,Mk}}{\mathcal{C}_{j,kM}\overline{x_1}(0)}-\overline{x_j}(M)\frac{s_j(M)}{s_j(0)}\right]$$

$$=-\mathcal{C}_{j,0M}\overline{x_1}(0)\left[\frac{n_j}{s_j(0)}-\overline{x_{j+1}}(M)\sum_{k=0}^{M}\frac{s_j(k)}{s_j(0)}\frac{\mathcal{E}_{j+1,Mk}}{\mathcal{C}_{j,kM}\overline{x_1}(0)}-\overline{x_j}(M)\frac{s_j(M)}{s_j(0)}+\overline{x_{j+1}}(M)\frac{s_j(M)}{s_j(0)}\frac{\mathcal{E}_{j+1,MM}}{\mathcal{C}_{j,MM}\overline{x_1}(0)}\right]$$

$$=-\mathcal{C}_{j,0M}\overline{x_1}(0)\left[\frac{n_j}{s_j(0)}-\overline{x_{j+1}}(M)\sum_{k=0}^{M}\frac{s_j(k)}{s_j(0)}\frac{\mathcal{E}_{j+1,Mk}}{\mathcal{C}_{j,kM}\overline{x_1}(0)}\right]-\mathcal{C}_{j,0M}\overline{x_1}(0)\frac{s_j(M)}{s_j(0)}\left[\overline{x_{j+1}}(M)\frac{\mathcal{E}_{j+1,MM}}{\mathcal{C}_{j,MM}\overline{x_1}(0)}-\overline{x_j}(M)\right]. \tag{B6}$$

Further, if a useful relationship is worth being noted

$$\overline{x_j}(M)=\xi_j-\alpha_j\hat{I},\quad j=2,...,r, \tag{B7}$$

we can rewrite Eq. (B6) in the final form

$$\begin{aligned}\frac{dn_j}{dt}=&-\frac{\mathscr{C}_{j,0M}\overline{x_1}(0)}{s_j(0)}\left[n_j-\xi_{j+1}\sum_{k=0}^{M}s_j(k)\,\frac{\mathscr{E}_{j+1,Mk}}{\mathscr{C}_{j,kM}\overline{x_1}(0)}\right]\\&-\hat{I}\left[\alpha_{j+1}\,\frac{\mathscr{C}_{j,0M}\overline{x_1}(0)}{s_j(0)}\sum_{k=0}^{M}s_j(k)\,\frac{\mathscr{E}_{j+1,Mk}}{\mathscr{C}_{j,kM}\overline{x_1}(0)}\right.\\&\left.-\frac{\mathscr{C}_{j,0M}s_j(M)}{\mathscr{C}_{j,MM}s_j(0)}\right]=I_j^{(2)}-d_j\hat{I}.\end{aligned} \tag{B8}$$

Here we use the notation $I_j^{(2)}$ for the quasisteady fluxes being represented in the form

$$I_{j+1}^{(2)}=L_{j+1}^{+}\overline{x}_1^{j+1}(0)-L_{j+1}^{-}n_j\overline{x_1}(0) \tag{B9}$$

with the nonequilibrium rates of association L_j^+ and dissociation L_j^- given by the formulas

$$\begin{aligned}L_{j+1}^{+}&=\frac{\mathscr{C}_{j,0M}}{s_j(0)}\,\frac{n_{je}}{(n_{1e}z_1(0))^j},\\L_{j+1}^{-}&=\frac{\mathscr{C}_{j,0M}}{s_j(0)},\quad j=2,...,r-1.\end{aligned} \tag{B10}$$

In order to cover $I_{r+1}^{(2)}$ by this definition we have to assume

$$L_{r+1}^{+}=\frac{1}{(n_{1e}z_1(0))^{r+1}},\quad L_{r+1}^{-}=\frac{1}{n_{r+1,e}}.$$

As far as the coefficients d_j are concerned they could be directly written with an eye to Eq. (B8)

$$\begin{aligned}d_j=&\left[\frac{\mathscr{C}_{j,0M}\overline{x_1}(0)\alpha_{j+1}}{s_j(0)}\sum_{k=0}^{M}s_j(k)\,\frac{\mathscr{E}_{j+1,Mk}}{\mathscr{C}_{j,kM}\overline{x_1}(0)}\right.\\&\left.-\frac{\mathscr{C}_{j,0M}s_j(M)}{\mathscr{C}_{j,MM}s_j(0)}\right],\quad j=2,...,r-1.\end{aligned} \tag{B11}$$

Note that in the equilibrium $I_j^{(2)}=\hat{I}=0$.

Finally, we should write the quasisteady equation for n_{r+1}, which can be easy obtained from two equalities

$$\frac{dn_{r+1}}{dt}=I_{r+1}-I_{r+2},$$

$$\frac{dn_r}{dt}=I_r-I_{r+1}.$$

Taking into account that $I_r\equiv\hat{I}$ and has already been found in the high-pressure limit $I_{r+2}=I_{r+2}^{(1)}$ we get

$$\frac{dn_{r+1}}{dt}=\hat{I}-I_{r+2}^{(1)}-\frac{dn_r}{dt}. \tag{B12}$$

4. Equations for monomers ($j=1$)

The last point is to get the quasisteady equations for $x_1(k)$, $k=1,...,M$. In doing that we shall consider the respective equations for the monomer populations Eq. (1) and take into account in the sums in Eq. (1) that for $k\neq 0$ it is reasonable to neglect condensation as compared with relaxation. In turn among all the relaxation terms we keep only leading terms with $j=1$. It is caused by the fact that for each j the corresponding term in these sums is of the order $\beta_j=n_{je}/n_{1e}\ll 1, j>1$.[32,12] Hence

$$\frac{dx_1(k)}{dt}=\Omega_k^c+\Omega_k^r,\quad k\neq 0. \tag{B13}$$

The RHS of Eq. (B13) contains only unknown populations $x_1(k)$, $k=0,...,M$. For $x_1(0)$ using the normalizing condition $\Sigma_{k,j}jx_j(k)=\text{const}$ we get

$$\begin{aligned}\frac{dx_1(0)}{dt}=&-\sum_{k=1}^{M_1}\frac{dx_1(k)}{dt}-\sum_{j=2}^{r}j\,\frac{dn_j}{dt}-(r+1)\,\frac{dn_{r+1}}{dt}\\&-(r+2)I_{r+2}^{(1)}-\sum_{j=r+3}^{N-1}I_j^{(1)}.\end{aligned}$$

Whence with allowance for Eq. (B12)

$$\begin{aligned}\frac{dx_1(0)}{dt}=&-\sum_{k=1}^{M_1}\frac{dx_1(k)}{dt}-\sum_{j=2}^{r-1}j\,\frac{dn_j}{dt}+\frac{dn_r}{dt}-(r+1)\hat{I}\\&-\sum_{j=r+2}^{N-1}I_j^{(1)}.\end{aligned} \tag{B14}$$

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