DIRECT SIMULATION MONTE CARLO STUDY OF THE FORMATION AND GROWTH OF CLUSTERS IN THE CASE OF VAPOR EXPANSION FROM A SUDDENLY SWITCHED SPHERICAL SOURCE

N. Yu. Bykov, G. A. Lukyanov,* and O. I. Simakova

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The processes of formation of silicon clusters in the case of vapor expansion from a suddenly switched spherical source into an ambient inert gas are considered. Vapor expansion and condensation are described by the direct simulation Monte Carlo method. A model of clusterization is proposed, which describes reactions leading to the growth and decomposition of clusters and corresponding energy-transfer processes. The main features of cluster formation in the case of vapor expansion into a gas are considered.

Key words: clusters, mathematical modeling, condensation, nanotechnology.

Introduction. Studying the formation and growth of clusters in the case of vapor expansion into a gas with a low pressure is important for various applications, which include, for instance, the synthesis of clusters and cluster materials from vapor produced by intense evaporation of condensed substances [1, 2]. Of significant interest, for example, are problems of expansion and condensation of vapor formed owing to laser evaporation of small solid particles of aerosols [3, 4]. In the general case, such problems are rather complicated, because the theoretical study should involve a large number of various interrelated physical processes, including radiation absorption, heating, melting, and evaporation of matter, and expansion of the resultant vapor with allowance for clusterization processes. As such problems are extremely complicated and involve many parameters, it is difficult to study the general laws of the processes of cluster formation owing to intense expansion of vapor. In addition to solving complicated realistic problems, therefore, it is also necessary to solve appropriate problems in simpler model formulations.

The present paper describes a model formulation of the problem of cluster formation in the case of expansion of silicon vapor generated by a suddenly switched spherical source (SSS) into a buffer gas (argon) under conditions typical of pulsed laser-induced ablation of small aerosol particles. The SSS model is one of the simplest models of unsteady gas dynamics and is widely used in studying relaxation processes in pulsed jet flows [5, 6]. Until now, the possibility of a detailed study of the processes of cluster formation and growth under the conditions of intense nonequilibrium expansion of vapor has been restricted by the lack of appropriate models of cluster formation, which would adequately describe these processes as a whole (beginning from the formation of dimers) with allowance for the set of elastic and inelastic interactions of vapor particles. Some variants of such models [7–9] based on the Direct Simulation Monte Carlo (DSMC) method and including the processes of particle collisions and energy exchange between the particles, which are described with different degrees of approximation, have appeared recently. The algorithm chosen in the present work for vapor motion calculations is the variant of the DSMC method used in [7, 10] for modeling expansion of the products of laser-induced ablation of a flat target. The model of cluster formation and growth proposed in [7] was used to calculate vapor expansion into vacuum. The present paper describes a complete model of clusterization in the case of vapor expansion into a low-pressure inert ambient gas.

*Deceased.
Mathematical Model and Formulation of the Problem. For modeling the flow of condensing vapor, we used the DSMC algorithm with a no-time-counter collision scheme [11]. The domain of simulations is the space between the evaporating spherical surface and the outer boundary located at a sufficiently large distance from the spherical surface: \( L = R_\infty - R_w \) (\( R_w \) is the sphere radius and \( R_\infty \) is the radius of the outer boundary).

The initial and boundary conditions are formulated as follows. At the initial time (\( t = 0 \)), the domain of simulations (\( r > R_w \)) is filled by the background gas (argon) with a concentration \( n_2 \) and temperature \( T_2 \); there are no vapor atoms in this gas. At \( t = 0 \), the gas (silicon atoms) starts to evaporate from the surface (\( r = R_w \)). The evaporation process is described by the Hertz–Knudsen law, which implies that the flux of evaporating silicon atoms is

\[
F^+ = \frac{1}{4} n_s u_{av} = \frac{p_s(T_w)}{(2\pi m k_B T_w)^{1/2}}.
\]

Here \( n_s \) and \( p_s \) are the concentration and pressure of saturated vapor at the surface temperature \( T_w \), \( u_{av} = (8k_B T_w/(\pi m))^{1/2} \) is the mean thermal velocity of evaporating atoms, \( k_B \) is the Boltzmann constant, and \( m \) is the atomic mass. The pressure \( p_s(T_w) \) is found from the Clapeyron–Clausius equation [12]. In the SSS model considered, the temperature \( T_w \) and, hence, the flux \( F^+ \) do not change with time.

For particles evaporating from the surface at \( t > 0 \), the velocity distribution function is assumed to be constant in time and to be semi-Maxwellian:

\[
f_w^+ = \frac{F^+}{2\pi} \left( \frac{1}{RT_w} \right)^2 \exp \left( -\frac{u_r^2 + u_\varphi^2 + v_\theta^2}{2RT_w} \right) = \frac{n_s}{(2\pi RT_w)^{3/2}} \exp \left( -\frac{u_r^2 + u_\varphi^2 + v_\theta^2}{2RT_w} \right), \quad u_r > 0.
\]

Here \( u_r, u_\varphi, \) and \( v_\theta \) are the components of the thermal velocity of particles and \( R \) is the gas constant. Particles returning to the source surface are excluded from the modeling process, which corresponds to the condition of their complete condensation. Particles that reach the outer boundary of the domain of simulations \( r = R_\infty \) are also excluded from the calculation (supersonic output boundary).

The clusterization model implies that all particles are neutral, and clusters are formed as a result of particle collisions. The model takes into account the following processes:

1) elastic collision of atoms \( A + A \rightarrow A' + A' \);
2) recombination of atoms \( A + A + A \rightarrow A'_2 + A' \);
3) association of a cluster and an atom \( A_i + A \rightarrow A'_k (k = i + 1) \);
4) association of clusters \( A_i + A_j \rightarrow A'_k (k = i + j) \);
5) evaporation of a monomer from a cluster \( A_k \rightarrow A'_{k-1} + A' \).

Here the primed quantities refer to particles after the collision; \( A \) stands for a silicon atom.

If there is also a buffer gas, the following reactions have to be taken into account:

— elastic collision of atoms of a buffer gas \( B + B \rightarrow B' + B' \);
— elastic collision of silicon atoms and buffer-gas atoms \( A + B \rightarrow A' + B' \);
— three-particle recombination \( A + A + B \rightarrow A'_2 + B' \);
— elastic collision of clusters and buffer-gas atoms \( A_k + B \rightarrow A'_k + B' \).

Here \( B \) stands for a buffer-gas atom.

Particle collisions are described by the hard sphere model. The parameters of the cluster \( A_k \) are the number of atoms \( k \), mass \( m_k \), radius \( r_k \), translational velocity \( u_k \), internal energy \( E_{int,k} \), and binding energy \( E_b(k) \). In accordance with the liquid spherical drop model [1], the cluster radius is determined by the formula

\[
r_k = r_w k^{1/3}, \quad r_w = (3m/(4\pi \rho))^{1/3},
\]

where \( r_w \) is the Wigner–Seitz radius and \( \rho \) is the density of the cluster-forming material.

The model considered implies that clusters possess completely excited rotational and vibrational degrees of freedom. The internal energy of the cluster \( A_k \) is presented in the form

\[
E_{int,k} = E_{r,k} + E_{v,k}, \quad E_{r,k} = \zeta_r k_B T_{r,k}/2, \quad E_{v,k} = \zeta_v k_B T_{v,k}.
\]

Here \( E_{r,k} \) and \( E_{v,k} \) are the energies of rotational and vibrational degrees of freedom, \( \zeta_r \) and \( \zeta_v \) are the numbers of rotational and vibrational degrees of freedom, and \( T_{r,k} \) and \( T_{v,k} \) are the rotational and vibrational temperatures of the cluster. For a dimer, we have \( \zeta_r = 2 \) and \( \zeta_v = 1 \); for other clusters, \( \zeta_r = 3 \) and \( \zeta_v = 3k - 6 \). It is assumed that \( T_{r,k} = T_{v,k} = T_{int,k} \) (\( T_{int,k} \) is the internal temperature of the cluster \( A_k \)).