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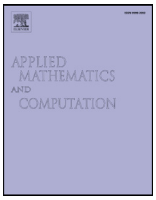

Mathematical models of water nucleation process for the Direct Simulation Monte Carlo method

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ABSTRACT

Two models of the nucleation process are developed on the basis of (a) size corrected classical nucleation theory and (b) kinetic approach within the Direct Simulation Monte Carlo method. Expressions for probabilities of cluster formation/decomposition reactions are proposed using the models for corresponding rate constants. Both models are employed for the direct simulation of stationary nucleation process in a spatially homogeneous water vapor, where the monomer parameters are kept constant. The relaxation of size distribution function of water clusters is computed for moderate supersaturation values and temperature of 320 K. Numerical analysis shows sufficient difference in results obtained within above mentioned models. The difference arises due to the incorrect description of the internal cluster temperatures caused by the limitation of the classical nucleation theory consisting in one-temperature approximation, which does not describe the details of the energy relaxation. The impact of the dimer formation mechanism (by triple and binary collisions) on cluster size distribution is also analyzed.

1. Introduction

Interest to the development of mathematical models and computation algorithms for calculation of formation and growth of water clusters in flows of different types is connected to the aerospace applications, such as spacecraft thruster plumes expansions into rarefied surrounding [1,2], natural phenomena such as jets in near-nucleus cometary atmospheres [3,4], etc. For simulation of such flows the approaches based on numerical solution of flow dynamics (Euler or Navier–Stokes) equations [5–8] or on the Direct Simulation Monte Carlo (DSMC) method [9], depending on the rarefaction in the stream, are widely used.

For the DSMC method several models of water cluster formation were proposed in the past few decades: (1) within the classical nucleation theory (CNT) [9–11], and (2) within the kinetic theory (KT) [11–14].

The most commonly used formulation of the CNT is based on the quasi-chemical model [6,15], within which forward/reverse processes of cluster growth/decay are considered as one monomer attachment/detachment to/from the cluster. Corresponding rate constants are variously parameterized, i.e. represented as functions of vapour temperature and supersaturation. Forward and reverse rate constants are connected by the mass action law. Equilibrium constants are calculated via

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the equilibrium cluster size distributions which are expressed via the Gibbs free energy. The Gibbs free energy is characterized via the surface tension. This makes the correct description of small-size clusters impossible.

Another limitation of the CNT consists in the fact that it can not be applied to flows with high supersaturations since it predicts the size of critical cluster less than unity. The size-corrected modification [16] of the CNT (SCCNT) can be used to avoid the above mentioned difficulties of the classical theory and can be adapted for DSMC calculations [17]. Instead of surface tension the SCCNT expresses the Gibbs free energy via a number of surface monomers of the cluster and the dimer equilibrium constant. The SCCNT, formulated on the basis of a quasi-chemical model, for its implementation requires the knowledge of rate constants for cluster growth/decay reactions and thermodynamic parameters of the vapor. Assuming that the mass action law is satisfied, rate constants for growth and decay are connected by the equilibrium constants, as it is in the CNT, but with the modified expression for the Gibbs free energy.

In this paper for the rate constants and equilibrium constants parametric representations as functions of temperature from [18,19] are used. Corresponding parameters can be obtained from comparison with the results of numerical or natural experiments.

For DSMC simulations the CNT scheme is modified. Since the publication [9] in 2004 it is a combination of classical nucleation and condensation theories (CCT). Within the classical condensation theory the equation for the cluster size distribution contains the source term $\rho_\Sigma^{-1} J\delta(r-r_*)$, where ρ_Σ is the overall mass density of gaseous and liquid phases, J is the nucleation rate, r is the cluster radius and r_* is its critical value. This term describes the clusters of critical size injection into the flux with the rate J. Clusters of subcritical size are not considered there, while the supercritical clusters are considered within the condensate fraction [20]. Within the proposed approach both condensation and evaporation are taken into account, i.e. the CNT is used to describe the evolution of clusters of critical size and of larger clusters. As follows from the CNT, the cluster-size distribution for the subcritical clusters is stationary, which means that the clusters of any size less than critical can be injected within such an approach. The reason why the clusters of critical size are injected consists in minimizing the computational costs: according to the CNT those clusters are the minimal that can be considered as stationary. As discussed in [21], non-stationary effects caused by the fast gas-dynamic variables evolution lead to the deviation of the fluxes in the cluster dimension space (g-mer formation rates J_g) from their stationary value J. Thus, the consideration of the whole set of the quasi-chemical model may be of a great interest.

Application of the DSMC approach to the condensation problem solution significantly extends the CNT capabilities. First of all it makes it possible to calculate all individual cluster characteristics and thus describe the non-equilibrium processes during condensation. Within the DSMC method the maximum cluster size is calculated. This allows to avoid the difficulty of summation of the infinite series of rates J_g in the equation for monomer (vapour) density or for the supersaturation [21].

The kinetic approach operates with probabilities of elementary collisional processes which describe cluster growth/decay. The probabilities are functions of individual particle properties: relative velocity of colliding partners, internal energies and a number of internal degrees of freedom. The majority of previously implemented DSMC algorithms based on KT use the simplest approximations [22–25] or molecular dynamic (MD) data [11] for determining the association probability for monomer-monomer and monomer-cluster collisions and the Rice–Ramsperger–Kassel (RRK) equation [19] for unimolecular cluster evaporation frequency [13,14,22–24]. Since those probabilities do not satisfy the microscopic reversibility principle, corresponding expressions for cross-section do not satisfy the detailed balance principle and therefore the equilibrium is shifted and the Hertz–Knudsen equation for large clusters is not reproduced. The above mentioned problem was avoided in paper [20], where RRK approach was used for describing both association and dissociation rate constants and expressions for high pressure parts of rate constants were written in a form which leads to the traditional equation for the equilibrium size distribution at the limit of high cluster size.

The first aim of this paper is to obtain expressions for probabilities and rate constants for water nucleation process and to apply them for simulations performed within the SCCNT- and KT-oriented models. Corresponding equilibrium constants should be in the agreement with the thermodynamic data and the model should reproduce equilibrium states correctly. The second aim is to analyze the role of different mechanisms of dimer formation in the nucleation process. In papers [11,13,14] only triple collisions of monomers forming dimers are considered. Triple collisions are simulated via two-step process: intermediate complex (dimer) formation and then, its stabilization by collision with the third particle. In paper [12] the formation of dimer via pair collision of monomers is considered. Here both processes are taken into account. The third and the main aim of the work is to perform series of computations for water nucleation process under stationary and spatially uniform conditions inserting proposed expressions for probabilities and rate constants in SCCNT and KT models and to compare results of simulations obtained within both these models.

The paper is organized as follows. After the discussion of the nucleation models in the Introduction, in Section 2 the reactions included into the nucleation model are described. Section 3 is devoted to the methodology of reaction rates approximation and calculation of corresponding probabilities. In Section 4 the results of simulations within the SCCNT and KT are discussed and further research is traced.

2. Reactions of cluster formation and decomposition

In this paper the quasi-chemical model forms the basis of both approaches: classical and kinetic nucleation theories. Within this model cluster growth/decay is described as a set of chemical reactions of clusters (g-mers) with monomers M_1.