

# Quasi-Chemical Cluster Model Approach To Gas Precondensation Stage

A.S.Artyukhin<sup>1</sup>, B.V.Egorov<sup>2</sup>, Yu.E.Markachev<sup>2</sup>, E.A.Plekhanov<sup>3</sup>, I.A.Ozarnov<sup>1</sup>

1- Moscow Institute of Physics and Technology (MIPT), Moscow, Russia

2- Central Aerohydrodynamic Institute (TsAGI), Zhukovsky, Russia

3- University of Salerno, Italy

**Abstract.** Quantum chemistry methods are used to calculate structure and energetics of clusters and to allow us to calculate equilibrium and rate constants of formation and destruction of clusters and then develop quasi-chemical cluster model approach to gas precondensation stage. The critical parameter of the theoretical model - mean statistical vibrational temperature of a cluster has been corrected by comparison with available experimental data of nucleation rate and the second virial coefficient and let us proved the theory by prediction of effective surface tension coefficient of water in good agreement with experiment.

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According to quasi-chemical cluster model (QCCM) a vapor consists of monomers and molecular associates – clusters (groups of monomers binding by molecular forces together). The growth of clusters is due to a monomer addition and the destruction is due to loss of a monomer. The chain of elementary processes of formation and destruction of a cluster  $A_n$  is given as [1]:



Here  $M$  – any molecule or cluster in gas phase;  $\tilde{K}_a(n)$  - the rate constant of a monomer addition to a cluster  $A_n$ ,  $\tilde{K}_d(n+1)$  - the rate constant of a cluster  $A_{n+1}$  dissociation on a cluster  $A_n$  and a monomer  $A_1$ . Cluster number density  $N_n(t)$  can be derived due to (1) from the following equation:

$$\frac{dN_n}{dt} = J_{n-1} - J_n, \quad (2)$$

where

$$J_n = N_1 N_n K_a(n) - N_{n+1} K_d(n+1), \quad (3)$$

Here  $J_n$  - the flux of clusters in the space of monomers in a cluster;  $K_a(n) = N_1 \tilde{K}_a(n)$ ,  $K_d(n+1) = N_1 \tilde{K}_d(n+1)$  (it is assumed that on initial stage of condensation (the stage of nucleation – precondensation)  $M = N_1$ ).

Eqs. (2) in quasi-equilibrium conditions  $\frac{dN_n}{dt} = 0$  is reduced to a system of inhomogeneous linear algebraic equations by  $N_n$  with the same  $J_n \equiv J_0$  in Eq. (3). In equilibrium conditions when all rates of forward and backward processes are balanced the system is reduced to homogeneous equations (3) with  $J_n \equiv 0$ .

Quasi-equilibrium distribution function  $N_n^0$  [2] depends on monomer number density, forward and backward rate constants of (1) and is derived from homogeneous equations (3). For the first step the calculations of structure and energetics of clusters have been carried out to calculate cluster reaction rate constants. Quantum-chemical calculations of clusters were made based on ab initio self-consistent field Hartree-Fock method with 6-311+G(d,p)

base functions. Electronic correlation corrections were made by the second order Moller-Plesset with the same basis [2]. PC adopted version of GAMESS code [3] was used for quantum-chemical calculations of clusters. The calculations did show that cluster geometrical parameters are found with great accuracy but the accuracy of calculation of energetic parameters (dissociation energy and the frequencies of intermolecular and intramolecular vibrations) is rather low. It is necessary to note that the calculation of structure and vibrational frequencies of clusters is carried out by normal mode method at  $T = 0K$  by finding the potential energy minimum for a system of particles in a cluster. The correct configuration of atoms with minimal potential energy depends on its zero-vibration energy and heat expansion of the cluster. That is why the correct frequencies of internal vibrations of a cluster prove to be the functions of temperature. These difficulties are overcome by so called *SCP* (self-consistent-phonon approximation) method or by the method taking into account the anharmonic additions to the potential of atoms interactions in a cluster [4].

Based on quantum-chemical calculations, normal vibration mode method basic structure and energetic characteristics of clusters were obtained and equilibrium constants, formation and dissociation of cluster reactions (1) have been calculated [2,5]. These calculations have let us derive quasi-equilibrium and quasi-stationary cluster distribution functions on sizes and calculate some thermodynamic and kinetic properties of clusters.

One of results [2] is analytic expression of dependence of number density of gas monomers with quantum characteristics of infinite size cluster at equilibrium state:

$$N_{1eq} = \frac{K_d(\infty)}{K_a(\infty)} = \lim_{n \rightarrow \infty} \frac{Q_1 Q_{n-1}}{Q_n} \frac{1}{P_1^0 V} = \lim_{n \rightarrow \infty} [K_p(n) kT]^{-1} \quad (4)$$

Here  $K_p(n)$  - equilibrium constant by pressure at formation of infinite size cluster. The introduction of so called mean statistical vibrational temperature of intramolecular vibrations in a cluster made it easy to theorize and allowed us to derive the expression for saturated vapor pressure [2]:

$$P_s \equiv P_\infty = CT^4 \left( 1 - \exp\left(-\frac{\bar{\theta}_\infty}{T}\right) \right)^6 \exp\left(-\frac{E_\infty}{T}\right) \quad (5)$$

$$\text{Here constant } C = \frac{2^6 \pi^5 k_B^4 m_{amu}^{3/2} A^{3/2}}{h^6 \sigma_1 [I_a(1) I_b(1) I_c(1)]^{1/2}}, (C_{H_2O} = 1.65 \cdot 10^3), E_\infty - \text{dissociation energy of infinite size}$$

cluster,  $\sigma_1$  - symmetry index of a monomer,  $I_a(1), I_b(1), I_c(1)$  - principal moments of inertia for a monomer,  $k_B, h, m_{amu}$  - fundamental constants,  $A$  - mass number for a monomer,  $\bar{\theta}_\infty$  - mean statistical vibrational temperature for infinite size cluster.

Mean statistical vibrational temperature for nonlinear cluster (e.g. water vapor cluster  $(H_2O)_n$ ) can be derived from the following expression:

$$\left( 1 - \exp\left(-\frac{\bar{\theta}_n}{T}\right) \right)^{6n-6} = \prod_{i=1}^{6n-6} \left( 1 - \exp\left(-\frac{\theta_i(n)}{T}\right) \right), \quad (6)$$

Here  $\theta_i(n)$  - vibrational temperature of  $i$ -th vibrational mode of  $n$  monomers cluster having  $6n-6$  intramolecular vibrational modes.

Analytic expression for calculating the nucleation rate  $J_0$  in explicit form is derived by using asymptotic solutions of the system (3) for quasi-equilibrium and quasi-stationary situations and asymptotic expressions for a number of cluster characteristics. This expression for water vapor is given as:

$$J_0 = 6.376 \cdot 10^{29} \frac{P_\infty^3}{T^{3/2}} n_*^{4.346} \frac{\left(1 + \frac{1}{n_*}\right)^{0.5}}{\left(1 - \frac{1}{n_*}\right)^{4.346}} (1 + n_*^{0.391})^2 \frac{\left[1 - \exp\left(-\frac{\bar{\theta}_\infty}{T}\right)\right]^{6n_*}}{\left[1 - \exp\left(-\frac{\bar{\theta}_n}{T}\right)\right]^{6n_*}} \times$$

$$\times \exp\left\{-\frac{\Delta E}{T} (n_* - 1)^\alpha - \frac{E_\infty}{T} + \frac{\Delta E}{T} \frac{\alpha(n_* + 3)}{(n_* - 1)^{1-\alpha}} - \frac{4.346(n_* + 3)}{n_*}\right\} \quad (7)$$

Due to Eq.(7), nucleation rate  $J_0$  depends on translational temperature  $T$ , saturation parameter  $S = \frac{P_{H2O}}{P_S}$ , saturated vapor pressure  $P_S$  (this parameter according to (5) depends on  $E_\infty$  and  $\bar{\theta}_\infty$ ),  $n_*$  - cluster critical size, mean statistical vibrational temperature of cluster  $\bar{\theta}_n$ , the difference of dissociation energy of infinite size cluster and that of a dimer  $\Delta E = E_\infty - E_2$  and parameter  $\alpha$ . The later parameters are involved in approximate expression for dissociation energy:

$$E_n[K] = E_\infty - \Delta E[(n-1)^\alpha - (n-2)^\alpha], n \geq 1, \alpha \in (0,1) \quad (8)$$

At  $\alpha = 2/3$  and  $\Delta E = 4\pi\sigma\left(\frac{3m}{4\rho}\right)^{2/3}$  Eq. (8) is reduced to classic expression

$E_{n+1} = E_\infty - 4\pi\sigma(r_{n+1}^2 - r_n^2)$ , where  $\sigma$  - surface tension coefficient,  $r_n$  - radius of a drop containing  $n$  monomers.

Eq. (7) is derived based on solution of algebraic equations set (3) and do not contain limitations dealing with continuity and differentiability of functions in Eq.(7). Critical cluster size  $n_*$  can be derived for given  $T$  and  $S$  as minimum of equilibrium distribution function by sizes  $N_n$  by simple enumeration process. By requiring the differentiability of  $N_n$  by  $n$  as continues argument the critical cluster size can be derived from the expression

$$\frac{dN_n}{dn} = 0 :$$

$$-\frac{\Delta E}{T} \alpha(n_* - 1)^{\alpha-1} + \ln(S) = -\frac{4.346}{n_*} + \frac{6(n_* - 1)}{T} \frac{(d\bar{\theta}_n/dn)_{n_*}}{(\exp(\bar{\theta}_{n_*}/T) - 1)}$$

$$- 6 \ln\left(\frac{1 - \exp(-\bar{\theta}_\infty/T)}{1 - \exp(-\bar{\theta}_{n_*}/T)}\right) \quad (9)$$

Expression (9) is an analog of classical relation between  $S$  and  $n_*$  by Gibbs-Thomson.

Here we decline some results of quantum-chemical calculations and obtain mean statistical vibrational temperature  $\bar{\theta}_n$  and its derivative  $\left.\frac{d\bar{\theta}_n}{dn}\right|_{n=n_*}$  based on comparison of theoretical expression  $J_0$  (7) with its experimentally measured value  $J_{0,\text{exp}}$ ; dimer dissociation energy  $E_2$  has been derived by experimental data of the second virial coefficient  $B(T)$ ;  $E_\infty$  and  $\bar{\theta}_\infty$  have been derived by experimental data of saturated water vapor pressures. The relationship between nucleation rate derivative by saturation  $\frac{d \ln J_0}{d \ln S}$  and cluster critical size  $n_*$  was found in experiment [7].

$$\frac{d \ln J_0}{d \ln S} = n_* + x, \quad (10)$$

where  $x = 1, 2$ .

By minimizing the functional:

$$\Phi(\chi, \eta) = \sqrt{0.5 \left[ \left( \frac{J_0 - J_{0,\text{exp}}}{J_{0,\text{exp}}} \right)^2 + \left( \frac{d \ln J_0 / d \ln S - n_*}{n_*} \right)^2 \right]}, \quad (11)$$

for given value of cluster critical size  $n_*$  and experimental value of nucleation rate  $J_{0,\text{exp}}$  the values of  $\chi = \bar{\theta}_{n_*}$  and  $\eta = \frac{d\bar{\theta}_n}{dn} \Big|_{n=n_*}$  have been found. Hence for given values of  $T$ ,  $S$ ,  $n_*$ , known parameters of  $E_\infty$ ,  $\bar{\theta}_\infty$ ,  $E_2$  and  $\alpha = 0.6125$  (this value was found for  $H_2O$  [2]) the values of  $J_0$ ,  $\bar{\theta}_{n_*}$  and  $\frac{d\bar{\theta}_n}{dn} \Big|_{n=n_*}$  have been found.

Fig.1 shows the results of nucleation rate calculation for different temperatures. Formula from [8] was used to represent experimental values of  $J_{0,\text{exp}}$ . Experimental nucleation rate is given by dash line; rhombs, squares, circles represent results of theoretical calculations by formula (7) with the values of  $\bar{\theta}_n$  and  $\frac{d\bar{\theta}_n}{dn}$  found from expression (11) for experiments [11]. The value of water vapor dimer dissociation energy  $E_2$  and  $\bar{\theta}_2$  have been found from comparison of theoretical value for the second virial coefficient derived from QCCM [10] and experimental data [9]:

$$B(T) = -K_p(2) = \frac{3.036 \cdot 10^4 \exp(E_2/T)}{T^4 (1 - \exp(-\bar{\theta}_2/T))^6} \quad (12)$$

The obtained values of  $\bar{\theta}_n$ ,  $\frac{d\bar{\theta}_n}{dn}$ ,  $E_2$  proved by calculations of effective surface tension coefficient [10], which was derived by equating equilibrium distribution functions – classical and derived by QCCM.

$$\sigma_{\text{eff}} = \frac{\Delta E(n-1)^\alpha}{4\pi n^2} - \frac{T}{4\pi n^2} \ln \left[ n^{3/2} \frac{\left( 1 - \exp \left[ -\frac{\bar{\theta}_\infty}{T} \right] \right)^{6n-6}}{\prod_{i=1}^{6n-6} \left( 1 - \exp \left[ -\frac{\theta_i(n)}{T} \right] \right)} \frac{R_n}{R_1} \frac{\sigma_1}{\sigma_n} \right], \quad (13)$$

where  $\sigma_1$ ,  $\sigma_n$  - symmetry indexes of monomer and cluster of size  $n$ ;  $R_n$ ,  $R_1$  - square roots from the products of principal moments of inertia of a cluster of size  $n$  and a monomer, respectively. Results of calculations of effective surface tension coefficient are given in Fig.2 as function of cluster size at translational temperature  $T = 297K$ . It is shown that effective surface tension coefficient reaches its classical value at  $n = 100$  with 0.3% discrepancy.

Another interesting fact is that classical Gibbs-Thomson function  $S(n_*)$  and the similar function obtained in QCCM have one mutual point. Calculated functions are shown in Fig.3, dash line – classical model (Gibbs-Thomson expression), solid lines – results of QCCM given at two translational temperatures  $T = 244K$  и  $T = 276K$ . At decreasing  $n_*$  the gap between  $S(n_*)$  curves, obtained in terms of QCCM and that of classical theory becomes significant (in classical model the size of a cluster is continuous variable). At increasing  $n_*$ , that is at decreasing saturation parameter  $S$ , the gap between these models is also observed because according to Gibbs-Thomson equation  $\lim_{S \rightarrow 1} n_* \rightarrow \infty$ . QCCM gives the finite value of  $n_*$  at  $S = 1$ , and also at  $0 < S < 1$ . It should be noted that

if  $n_*$  is finding by direct numerical procedure of seeking the minimal value of quasi-equilibrium cluster size distribution function instead of using Eq.(9) then discrete character of dependence  $n_*$  on  $S$  is revealed. Developed QCCM tuned according to available experimental data (nucleation rates  $J_0$ , the second virial coefficients  $B(T)$ ) allows to obtain a number of useful correlations, e.g. dependence of isobaric specific heat capacity  $C_p$  on temperature  $T$  and pressure  $P$ .

The results of experimental measurements of methane pressure dependence on temperature at different densities are shown in Fig.4 (solid lines, densities (kg/m<sup>3</sup>): 1 – 195.22, 2 – 169.37, 3 – 155.13, 4 – 139.799, 5 – 103.716, 7 – 52.941). The results of calculation based on quasi-classical model by Stogryn-Hirschfelder [12] are depicted by dash lines (6,8). It is shown that the simplest cluster model is able to represent results in good accordance with experiment. Hence more sophisticated QCCM can be used to treat the similar experimental data to obtain good agreement between theory and experiment.

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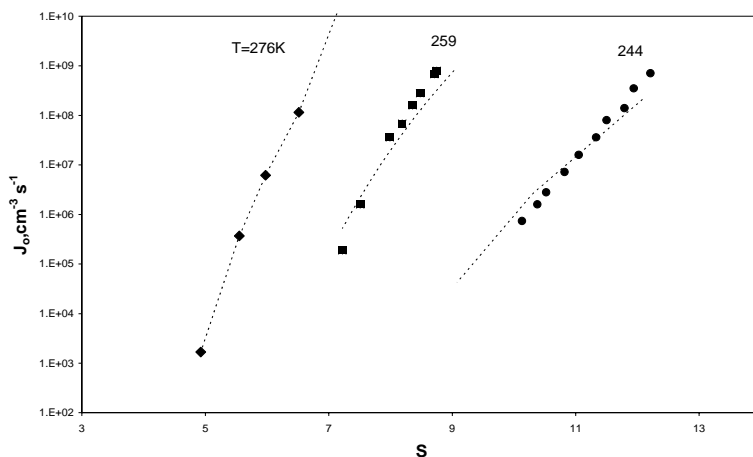


FIGURE 1.

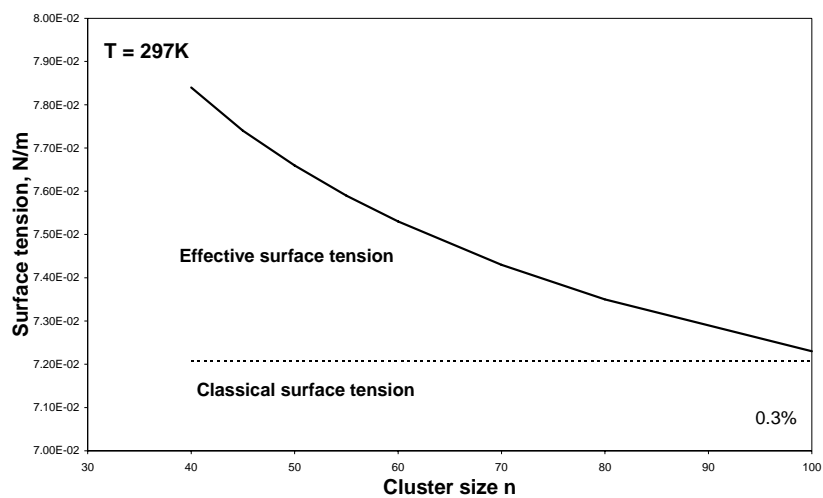


FIGURE 2.

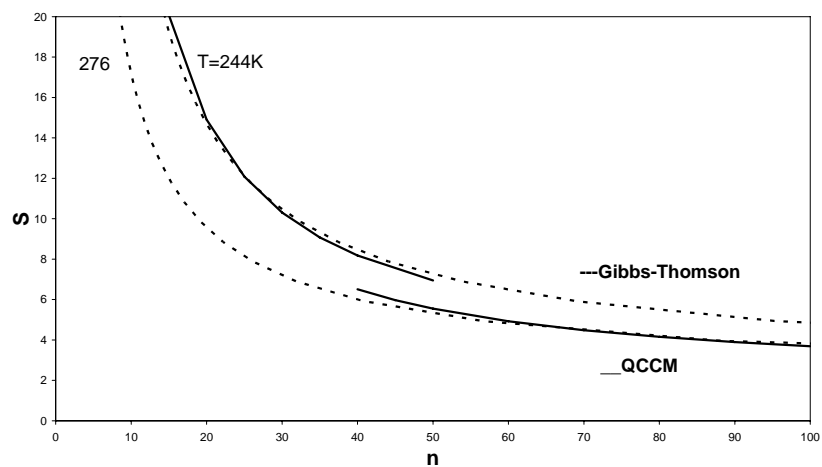


FIGURE 3.

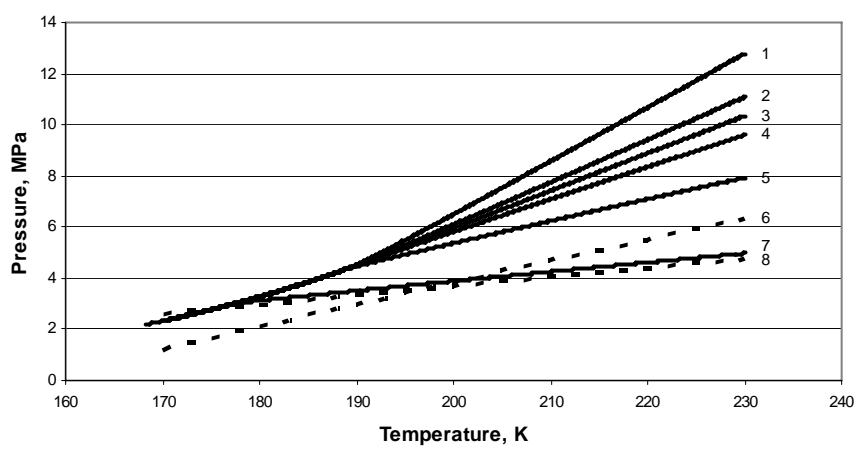


FIGURE 4.