Kinetic Theory of a Carrier Gas Effect on Nucleation in Diffusion Chambers

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Abstract. Kinetic theory is presented which proposes an explanation of a carrier gas effect on nucleation in DCC. The main idea of this theory is that for DCC transport of condensing molecules to the cluster surface is determined by their diffusion through a carrier gas that results in new kinetic equations or, in other words, in usual kinetic equations where rate constants of the cluster formation depends upon carrier gas pressure. Analytical dependencies of critical supersaturation S_* and derivative $\partial S_*/\partial T$ on a carrier gas pressure P_0, temperature T and the nature of the carrier gas are derived that reproduce experimental data of Heist and co-authors.

MAIN IDEA OF THE THEORY

First we have to discuss the main physical idea of our theory that in more detail is given in [1]. We consider nucleation process when a certain molecule attaches a cluster. In the existing theories usually rate constant of this process is not supposed to depend on any characteristic (for instance, pressure) of background gas. This is true unless transport of this molecule to the surface of the cluster is regulated by diffusion of the molecule through the background gas, and the rate of chemical reaction (attachment of the molecule to the cluster) is much more than the rate of diffusion. As shown in [1] typical conditions in DCC just meet these requirements and hence this is the case when nucleation kinetics is a diffusion-limited one.

In a bit more detail, if a certain cluster with j molecules transits to another sort with $j+1$ molecules by attaching a monomer the rate of this process K_j^+ in a usual nucleation theory is proportional to the free-molecular flux of monomers on the surface of this cluster, and this flux is determined by the numerical concentration of monomers. Under conditions of DCC this assumption stops to be valid because the real concentration of monomers at the external boundary of the Knudsen layer over the cluster surface differs from the concentration n_1 determined far from the cluster because of the presence of the background gas. It is caused by the existence of a concentration jump in the vicinity of the cluster surface, and the value of this jump becomes considerable when the mean free path of the condensing molecules in the carrier gas is of order of the cluster radius.

As for DCC the number density of the background gas n_0 is few orders more that the number density of the vapor n_1, the mean free path of the vapor molecule in the own vapor λ_v is about two orders more in length than the mean free path of this

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molecule in the carrier gas λ_{vg}. That is why in the vicinity of the cluster surface where we should determine K_j^+ vapor molecules collide only with the carrier gas ones and therefore there is reason to expect vapor concentration n_v to be equal to n_1 if the number of such collisions is high. Taking this effect into account we could obtain the following new representation for K_j^+ [1]

$$K_j^+ = \nu_j^+ \frac{S\Theta_j + 1}{S(\Theta_j + 1)} \approx \nu_j^+ \frac{S\Theta_j + 1}{S}, \quad \Theta_j \,?\, 1$$

$$\Theta_j \approx \Theta j^{-1/3}, \quad \Theta = \frac{3}{2\pi^2 (1 + C/T)} \frac{k_B T}{P_0 \sigma_{vg}^2} \left(\frac{4\pi\rho_l}{3m_1} \right)^{1/3}$$

Here S is supersaturation, C is the Sutherland constant, m_l is a vapor molecular mass, ρ_l is liquid density, k_B is the Boltzmann constant, $\pi\sigma_{vg}^2/4$ is a collision cross-section of the vapor and gas molecules, therefore σ_{vg} is approximately a half of the sum of effective diameters of the vapor and gas molecules. We also introduced notation ν_j^+ for the traditional (kinetic) rate constant that is proportional to square of the droplet radius and Θ_j is our correction for the case of the diffusion-limited kinetics. As follows from analysis of [1] $\Theta_j < 1$ and is inversely proportional to P_0 - the pressure of the carrier gas because the diffusion coefficient is inversely proportional to P_0. In contrast the rate constant of the inverse process K_j^- does not depend on the external environment of the cluster and is determined only by intracluster processes.

SOLUTION OF KINETIC EQUATIONS

Despite we derived a new representation for the cluster formation rate constant which now depends on the background gas pressure we can not proceed just substituting this expression into the nucleation rate, for instance, provided by classical nucleation theory. Rather, we need to reconsider kinetic equations describing transport and nucleation of vapor in DCC and try to find their solutions. According to our microscopic nucleation theory (MNT) [2] a studying mixture of gases and clusters is treated as a mixture of ideal gases each of that is characterized by the size of the identical clusters composing it. Continuity and diffusion equations for the mixture components obtained in the Navier-Stokes approximation are used, that based on the analysis of the DCC operation specificity and our asymptotic method [1,3] we managed to analytically solve, obtaining the following representation for concentrations n_j of clusters with j molecules

$$n_j \approx n_{ye} S \prod_{i=1}^{j-1} \frac{i^{1/3} + S\Theta}{i^{1/3} + \Theta}, \quad j \le y$$

$$n_j \approx n_{je} S^y \prod_{i=1}^{y-1} \Theta_i \prod_{k=y}^{j-1} \frac{\dfrac{\partial \ln K_{j+1}^+}{\partial j} + \dfrac{\partial \ln n_{je}/n_{j+1,e}}{\partial j}}{\dfrac{\partial \ln K_{j+1}^+}{\partial j} + \dfrac{\partial \ln \Theta_j}{\partial j}}, \quad j > y$$

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Here n_{je} is the equilibrium concentration [2], parameter y is introduced as a cluster size being a boundary between two kinds of solution. In [1] an equation for y is derived which takes a simple form if S exceeds approximately 1.5 (as it usually takes place in a zone of active nucleation in experiments in DCC)

$$\frac{2b}{3y^{1/3}} - \ln\left(\frac{S\Theta_j + 1}{1 + \Theta_j}\right), \qquad b = \frac{4\pi\sigma}{k_B T}\left(\frac{3m_1}{4\pi\rho_l}\right)^{2/3}$$

where σ is surface tension. At $\Theta_j \cong 1$, y coincides with the critical size.

DERIVING OF NUCLEATION RATE MEASURED IN DCC

To understand what is the nucleation rate measured in the experiment we use the following consideration. At the initial stage of the DCC work a certain quasisteady distribution of clusters is formed corresponding to the established distribution of S and T over the height of DCC. After that clusters (droplets) start to move due to gravity, the drag and thermophoretic forces that results in a violation of this quasisteady distribution. A certain amount of clusters reaches zone D where they are detected. Thus all clusters capable to fall down or to reach the top wall leave the zone of active nucleation.

If nucleation stopped, only these falling droplets would be registered during a short period of time while after this period no droplets should be visible (all of them reach either the bottom or top plates). The flux of droplets per unit square per unit time is $v_g n_j$, where n_j is their concentration and v_g - velocity of the clusters' precipitation. However, experimentalists present another value - the number of droplets per unit volume per unit time. For instance, it could be find by counting the falling drops within a certain (apparently rather long) period of time and then divide this number of droplets by the time, the square of the chamber and the width of the laser beam. If the period of detection is more than the time necessary for droplets to reach the bottom plate but the droplets are still detected, it means that due to transport of vapor molecules to clusters (diffusion) and chemical reactions between them (nucleation) the quasisteady distribution of clusters is restored and anew formed droplets fall down following the previous ones. In what follows the process is frequently repeated.

Based on this consideration we obtained for the nucleation rate J [3]

$$J \approx A(T_*)\left[\exp(-by^{2/3})\prod_{j=1}^{y}\frac{S\Theta + j^{1/3}}{\Theta + j^{1/3}}\right]^2 j_d^{2/3} S^2 K_{y+2}^{-}\frac{2b}{9y^{7/3}} \qquad (1)$$

where $A(T)$ is a preexponent of the equilibrium cluster distribution [2], and expression for j_d is given in [3]. For some regimes $j_j < y$.

EFFECT OF A CARRIER GAS

Now we can put $J = 1$ drop/sec/cm^2 as say in experiments of Heist [4,5] and differentiate both sides of (1) on T at $P_0 = const$ or on P_0 at $T = const$ to reveal how maximum supersaturation depends on T or P_0 or even on the nature of the carrier gas.

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The results are the following [3] (we mark parameters in maximum nucleation plane by subscript $*$).

- S_* linearly increases as P_0 increases at $T_* = const$ that reproduces the available experimental data of [4-6];
- Critical supersaturation S_* increases as T_* decreases at $P_0 = const$ (also in accordance with the experiments);
- If under conditions of DCC $S\Theta \cong 1$ then $S\Theta = c(T)$ and y depends only on T and does not depend on P_0 and S. In such a case function $\partial \ln S_*/\partial T$ does not depend on P_0. Moreover, as $S_* \propto P_0$ one has $\partial S_*/\partial T \propto P_0$.
- The slopes of the straight lines $S_*(P_0)$ decrease as the temperature T_* increases.
- The heavier the carrier gas the more is the efficient diameter of its molecule and hence the more pronounce dependence of S_* on P_0 occurs as well as the slopes of the lines $S_*(P_0)$ increase. This fact is also in good qualitative agreement with the experimental data of [4].
- As the molecular mass of the molecule of the condensing vapor decreases usually it gives rise to the decrease of the carrier gas effect. Such a situation has also been observed in many experiments.

The main conclusion which is made here based on the results obtained is that the dependence of S_* on P_0 observed in the experiments in DCC has no connection with the nucleation kinetics itself and is determined by the peculiarities of the transport processes in DCC.

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