On the kinetics of condensation through homogeneous nucleation

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(28. VIII. 1980; rev. 13. I. 1981)

Abstract. A theory of condensation through homogeneous nucleation in a Wilson chamber is developed. We show that a partly analytic treatment, allowing a considerable reduction of numerical expenditure, is possible if supersaturation varies slowly in time. In this *quasistationary* approach, the initial nucleation rate I_0 can be calculated from the total number of produced droplets. This may perhaps yield new means for the experimental determination of I_0.

I. Introduction

'The central question of nucleation theory is quite simple. Experimentally, it is observed that a vapour can be kept slightly supersaturated almost indefinitely without condensation of the vapour. Then if the supersaturation is slowly increased, at some critical supersaturation, an abundance of small droplets will be quite suddenly produced and condensation will follow. The question which nucleation theory attempts to answer is 'At what critical supersaturation does this onset of condensation occur?'' [1].

One generally accepts that this question is answered by a theory of the stationary nucleation rate. Such theories were developed [2, 3] and they predict correctly the strong increase of the nucleation rate with supersaturation. But major discrepancies occur concerning the absolute value of the nucleation rate at a given degree of supersaturation, both between theory and experiment and between different theories. To overcome these difficulties is the main goal of current research in nucleation theory [4, 5].

The motivation to the present study is an uneasiness we felt about two facts: First, the easiest way to define *experimentally* a 'critical supersaturation' consists in observing the so-called fog limit, the point at which the density of water droplets and their sizes are big enough to allow visual observation. To describe this phenomenon, it is clearly not enough to know the stationary nucleation rate. One also needs some insight into the dynamics of the condensation process, how fast the droplets grow once they are created. Moreover, the concept of the fog limit is rather hard to specify theoretically despite its experimental usefulness. Secondly, it is possible to measure directly the stationary nucleation rate and to avoid so the concepts of the fog limit or of the critical supersaturation. But these experiments are extremely difficult to perform and give at most an order of

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magnitude of the nucleation rate. We hoped that a study of the dynamics of condensation through homogeneous nucleation would clarify the notion of the critical supersaturation and indicate perhaps easier means to measure the stationary nucleation rate.

In what follows, we establish a theory of condensation through homogeneous nucleation for a Wilson chamber. In doing so, one is faced with the problem to determine explicit solutions of the kinetic equation for homogeneous nucleation if the supersaturation varies in time. Clearly, this is only possible by introducing further simplifying assumptions for instance that the supersaturation varies *slowly*. A careful discussion of the stationary solution of the nucleation equation (Chapter II) provides us with a criterion of quasistationarity (equations (21) in Chapter III). Under the condition of quasistationarity, the droplet distribution for droplets of smaller size than about twice the critical one equals the stationary distribution belonging to the momentary value of the supersturation and the nucleation rate has the corresponding stationary value. As for the bigger droplets, the quasistationary time evolution of the droplet spectrum is described by a quasilinear partial differential equation the solution of which can be reduced to the integration of an ordinary first order differential equation.

We get a closed system of equations of motion for the supersaturation by specifying the physical process conditions. In our theory of condensation through homogeneous nucleation for a Wilson chamber we assume that pressure and temperature are held constant. The resulting equations of motion for the supersaturation are solved numerically.

The results are discussed in Chapter IV. We show that the system exhibits a well defined nucleation time t_n such that practically all droplets (about 90%) are created before the time t_n and with an approximately constant nucleation rate. Up to then, the supersaturation has lowered less than 1% from its initial value. Thus, only a small part of the vapour has condensed at time t_n, i.e., condensation starts after nucleation has ceased and the temperature change by the heat of condensation is negligable for nucleation.

It is an important feature of our theory that the nucleation time t_n can be calculated explicitly – it is essentially a function of the initial nucleation rate I_0 – without use of the numerical solution. The total number of droplets at the end of the nucleation process is given by the product $I_0 t_n$. One can, thus, determine the initial nucleation rate I_0 from the total number of produced droplets (Chapter V). We think that to be quite a general feature of condensation through homogeneous nucleation although the analytic form of this connection depends upon the chosen process conditions. It opens perhaps new experimental ways to measure the nucleation rate I_0.

II. The principles of nucleation kinetics

A. Our discussion of nucleation kinetics begins with the equilibrium properties of fog. The starting point is an idea due to J. Frenkel: The pure vapour phase does not represent the true thermodynamical equilibrium – droplets of the liquid phase are always present. One may consider droplets of a given size as molecules of a new substance which contribute a mixing term to the entropy of the system, thus compensating the positive energy of formation [3].

This remark is valid quite independently from the precise physical nature of the 'droplet' – one only must require the possibility to define thermodynamic potentials for such 'droplets'; the atmosphere is acting as a heat bath. This thermodynamic potentials can then be used as building blocks for the Helmholtz free energy of (dilute) fog (we follow [6]):

$$F = F_0(V_0, N_0, N_B, T) + \sum_{x=2} N_x \cdot (F_x(V_x, T; V_0, N_0)$$
$$+ kT \cdot (\ln N_x - 1)). \tag{1}$$

F_0 denotes the Helmholtz free energy of the atmosphere depending upon its volume V_0 its water particle number N_0 and the particle number of a inert component B ('air'). N_x denotes the number of droplets containing x water molecules and F_x the Helmholtz free energy of a x-droplet in contact with the atmosphere and moving freely in the volume V_0.

Formula (1) gives the Helmholtz free energy of fog with the restriction that the particle numbers N_0, N_x and the volumes V_0, V_x are fixed. The equilibrium distribution is determined by the minimum of F with respect to a variation of the parameters N_x and V_x the total number of water molecules and the total volume V of the system being constant. The result is ([6], formula (II.6d)):

$$\frac{1}{V} N_x(\text{equilibrium}) \equiv \lambda_x = \frac{1}{V} \exp\left(\frac{x\mu - G_x}{kT}\right) \tag{2}$$

where λ_x is the equilibrium number per volume unit of droplets with x molecules of water, μ is the chemical potential per water molecule of the total system air + vapour + droplets (it is very close to the chemical potential μ_v of the vapour) and G_x denotes the Gibbs potential of a droplet containing x water molecules $(G_x = F_x - V_x \partial F_x/\partial V_x)$.

The most simple phenomenological ansatz for the Gibbs potential G_x of a spherical droplet is the following ([6], Chapter III.2):

$$G_x = -kT \ln \frac{V}{V^*} + x\mu_l + 3\left(\frac{4\pi}{3}\right)^{1/3} \sigma v_l^{2/3} x^{2/3} \tag{3}$$

leading to the equilibrium distribution

$$\lambda(x, a) = \frac{1}{V^*(x)} \exp\left(ax - \tfrac{3}{2}bx^{2/3}\right) \,^2) \tag{4}$$

where

$$a = \frac{\mu_v - \mu_l}{kT} = \ln S$$

and

$$b = 2\left(\frac{4\pi}{3}\right)^{1/3} \frac{\sigma v_l^{2/3}}{kT}$$

(μ_l: chemical potential per molecule of the liquid water, v_l: volume per molecule

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[2])   In [6, 8] we use $\alpha = -a$, $\gamma = 3b/2$ instead of a and b. λ_x denotes there the *total* number of droplets in the system containing x molecules of water.

of the liquid, σ: surface tension of the liquid–vapour interface). This ansatz accounts for the finiteness of the droplet and for its interaction with the atmosphere through a surface term. Our supersaturation parameter a is the logarithm of the supersaturation ratio S. Numerical values of b for the system water–air are given in Appendix B.

The quantity V^* includes all contributions to G_x which are not proportional to the volume or to the surface of the droplet. It also takes into account the fact that the integration over the coordinates of the centre of mass of each droplet can be carried out when one calculates the partition function of fog yielding the term $-kT \ln V$ in formula (3). One must thus calculate the partition function for the single droplet under the restriction of a fixed centre of mass.

The important requirements on formula (4) are that it correctly describes the dependence upon the supersaturation and that one can consider V^* as a slowly varying function of x – slowly varying with respect to $\exp(ax - \frac{3}{2}bx^{2/3})$. We stress the fact that this can only be expected if x is not too small. We will assume this to be true for $x \geqslant 30$. The problem of calculating the function $V^*(x)$ (the problem of the 'replacement' free energy – see [7] for a survey) is extremely hard because it implies the calculation of the partition function of a finite droplet. We shall see, however, that we only need one value of this function which we shall introduce as a phenomenological parameter.

B. Let us now discuss the kinetics of droplet formation. We consider a droplet containing x water molecules as a molecule of a substance A_x and consequently describe the formation and the growth of the droplets by a set of chemical reactions. We take only two of the many possible types of chemical reactions into account:

i) successive accumulation or evaporation of single water molecules from the droplets

$$A_1 + A_x \leftrightarrow A_{x+1}, \qquad x \geqslant 2$$
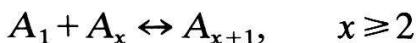
ii) direct formation of droplets out from the vapour

$$xA_1 \leftrightarrow A_x, \qquad x \geqslant 2.$$
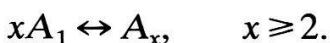
We neglect for instance reactions of the type $A_x + A_y \leftrightarrow A_{x+y}$ or $xA_1 + A_y \leftrightarrow A_{x+y}$ $(x, y \geqslant 2)$ expecting the reactions i) and ii) to be the most frequent ones at least in a vapour which is not too dense and at the beginning of the nucleation process. Collisions between droplets, although they may be effective in building up big droplets, do not change directly the supersaturation of the atmosphere – one reason more to neglect them for the present purpose.

The expression (1) of the Helmholtz free energy of fog corresponds to an ideal mixture with respect to the particle numbers N_x of the droplets. The considerations of the Appendix A can, thus, be applied yielding the following set of kinetic equations for the particle number densities n_0 of the vapour and n_x of the droplets:

$$\dot{n}_0 = - \sum_{x=2} (\dot{\phi}_x^{(1)} + x \cdot \dot{\phi}_x^{(2)}) \tag{5a}$$

$$\dot{n}_2 = -\dot{\phi}_2^{(1)} + \dot{\phi}_2^{(2)} \tag{5b}$$

$$\dot{n}_x = -(\dot{\phi}_x^{(1)} - \dot{\phi}_{x-1}^{(1)}) + \dot{\phi}_x^{(2)}, \qquad x \geqslant 3 \tag{5c}$$

where the time derivatives of the reaction parameters $\phi_x^{(1)}$ $\phi_x^{(2)}$ of the reactions of type i) and ii) are given by

$$\dot{\phi}_x^{(1)} = c_x^{(1)} n_0 n_x - e_x^{(1)} n_{x+1} = c_x^{(1)} n_0 \lambda_x \left(\frac{n_x}{\lambda_x} - \frac{n_{x+1}}{\lambda_{x+1}} \right) \tag{6a}$$

$$\dot{\phi}_x^{(2)} = c_x^{(2)} n_0^x - e_x^{(2)} n_x = c_x^{(2)} n_0^x \left(1 - \frac{n_x}{\lambda_x} \right). \tag{6b}$$

The static distribution λ_x is given by equation (2). This follows from the definition (A4) of the activities and from equation (1):

$$\alpha_x^{(2)} = \frac{\partial F}{\partial N_x}\bigg|_V - x \frac{\partial F}{\partial N_0}\bigg|_V = G_x + kT \cdot \ln N_x - x \cdot \mu$$

$$\alpha_x^{(1)} = \alpha_{x+1}^{(2)} - \alpha_x^{(2)}.$$

Considering x as a continuous variable we get the following partial differential equation for the time evolution of the droplet distribution $n(x, t)$:

$$\frac{\partial}{\partial t} n(x, t) = \frac{\partial}{\partial x} \left(D(x) \lambda(x, a(t)) \frac{\partial}{\partial x} \frac{n(x, t)}{\lambda(x, a(t))} \right)$$

$$+ C \cdot \delta(x - 2^+) \cdot \left(1 - \frac{n(x, t)}{\lambda(x, a(t))} \right) \tag{7}$$

with $D(x) = c_x^{(1)} n_0$ and $C = \sum_{x=2} c_x^{(2)} n_0^x$. The symbol $\delta(x - 2^+)$ indicates a δ-function with support near the lower end of the interval $[2, \infty)$.

The kinetic equation has the form of a continuity equation with a source term. The first expression on the right hand side of equation (7) is the negative divergency of a 'current' $-D\lambda \, \partial_x(n/\lambda)$ which is nothing else than $\dot{\phi}_x^{(1)}$. It accounts for the chemical reactions of type i) which do not change the total number of droplets. Thus, the boundary condition of the function $n(x, t)$ at $x = 2$ has to be as follows:

$$D(x) \lambda(x, a(t)) \frac{n(x, t)}{\lambda(x, a(t))}\bigg|_{x=2} = 0. \tag{8a}$$

For $x \to \infty$ we may choose

$$\lim_{x \to \infty} n(x, t) = 0. \tag{8b}$$

The source term stems from the reactions of type ii) which produce new droplets. (It is often not remarked that the contribution of the chemical reaction $A_1 + A_1 \leftrightarrow A_2$ to the nucleation equation has an analytical form very different from the contribution of the reactions $A_1 + A_x \leftrightarrow A_{x+1}$ with $x \geqslant 2$.) We assume that the direct formation of droplets is important only for the very smallest ones; we expect $c_x^{(2)} n_0^x$ to be a rapidly decreasing function of x. The quantity C is the total production rate per unit volume of droplets from the vapour. The nucleation rate

$$\frac{d}{dt} \int_2^\infty dx \, n(x, t) = C \cdot \left(1 - \frac{n(2, t)}{\lambda(2, a(t))} \right)$$

is smaller than C because a part of the created droplets reevaporate.

The function $D(x)$ has the form (see [8], II.2 and III.4)

$$D(x) = E \cdot x^{2/3}/(1+(x/x_c)^{1/3}) \tag{9}$$

where

$$E = 3\left(\frac{4\pi}{3}\right)^{1/3} \cdot v_l^{2/3} \cdot w \cdot n_s \sqrt{\frac{kT}{2\pi m}},$$

$$x_c = \frac{4\pi}{3v_l}\left((L_D/w)\sqrt{\frac{2\pi m}{kT}}\right)^3.$$

v_l denotes the molecular volume of the liquid, m its molecular mass, n_s the saturation particle density of the vapour, w the absorption probability of a vapour molecule hitting the liquid surface, L_D the coefficient of particle diffusion of the vapour. x_c accounts for a diffusional accommodation effect.[3] Numerical values of E and x_c are given in Appendix B.

The kinetic equation (7) with the boundary conditions (8) is discussed in [8] under the condition of constant supersaturation. The stationary nucleation rate per unit volume $I(a)$ is calculated ([8], Chapter III.3):

$$I(a) = \left(\int_2^\infty \frac{dx}{D(x)\lambda(x, a)} + \frac{1}{C}\right)^{-1}.$$

In this paper we only consider the limit $C^{-1} \to 0$. We neglect that the nucleation rate saturates at the total production rate C. This means that we assume a sufficiently high vapour density ($C \sim n_0^2$!). In this limit we have:

$$I(a) = \left(\int_2^\infty \frac{dx}{D(x) \cdot \lambda(x, a)}\right)^{-1} \tag{10}$$

which is the usual result.

The stationary droplet distribution $n_{st}(x, a)$ is given by ([8], Appendix C):

$$n_{st}(x, a) = I(a) \cdot \lambda(x, a)\int_x^\infty \frac{dy}{D(y)\lambda(y, a)}. \tag{11}$$

The properties of the static distribution function $\lambda(x, a)$ are well known (see Fig. 1). It has a sharp minimum at Kelvin's critical size x^* determined by the minimum of the exponent of equation (4):

$$x^* = (b/a)^3. \tag{12}$$

(The function $V^*(x)$ is slowly varying compaired with the exponential!)

The function $D(x)$ is slowly varying too and the integrand of formula (10) has a sharp maximum at $x = x^*$. This integral can, thus, be calculated by the method of the steepest descent yielding ([8], Chapter III.4):

$$I(a) \cong \frac{E}{V^*} \sqrt{\frac{b}{6\pi}} \exp\left(-\tfrac{1}{2}b^3/a^2\right) = E\sqrt{\frac{b}{6\pi}} \lambda(x^*, a) \tag{13}$$

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[3]   We recalculated the quantity x_c taking into account also thermal accommodation. The result of this rather tough calculation is that thermal accommodation is less important than diffusional accommodation for temperatures below 310°K because the saturation density n_s of the vapour is then low.
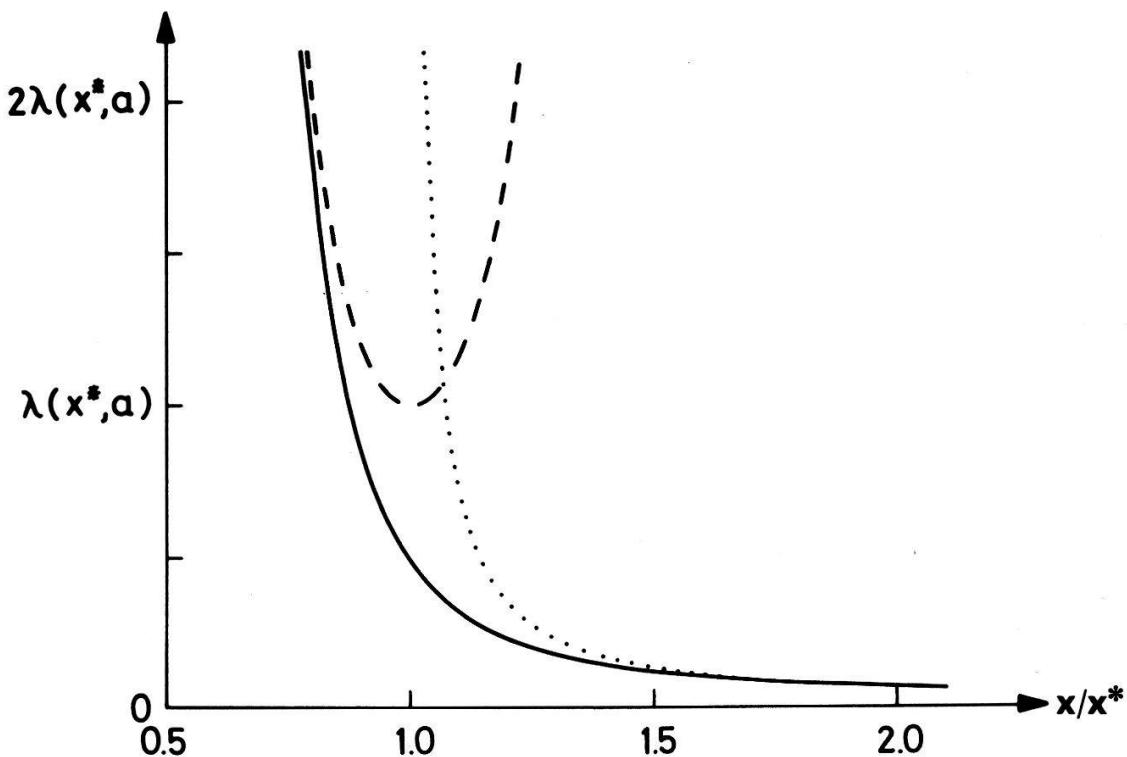
Figure 1
The static droplet distribution $\lambda(x, a)$ (dashed line) and the stationary distribution $n_{st}(x, a)$ (full line) for a fixed value of a. The dotted line indicates the upper bound (16c) of n_{st}.

where

$$V^* := V^*(x^*). \tag{14}$$

We neglected the factor $1 + (x^*/x_c)^{1/3}$ in the function $D(x^*)$ because $(x^*/x_c)^{1/3} < 10^{-4}$ in our example. Numerical computation shows that the approximation (13) is better than 1% for $\frac{1}{2}ax^* > 10$.[4]

The nucleation rate depends very sensitively on the supersaturation parameter a:

$$\frac{I(a - \delta a)}{I(a)} \leq e^{-x^* \cdot \delta a} \tag{15}$$

if $a \geq \delta a \geq 0$. x^* lies typically between 40 and 100.

The stationary nucleation rate n_{st} shows the following behaviour:

$$n_{st}(x, a) \simeq \begin{cases} \lambda(x, a) & \text{if} \quad x \ll x^* & (16a) \\ \frac{1}{2}\lambda(x^*, a) & \text{for} \quad x = x^* & (16b) \\ I(a)/(D(x) \cdot (a - bx^{-1/3})) & \text{if} \quad x > 2x^* & (16c) \end{cases}$$

The last expression is an upper bound of n_{st} for all $x \geq x^*$ which becomes almost identical with n_{st} for all $x > 2x^*$ (see Fig. 1). This bound follows from the inequality

$$\frac{1}{D(y)\lambda(y, a)} \leq \frac{1}{D(x)\lambda(x, a)} \exp\left(-a \cdot (1 - (x^*/x)^{1/3}) \cdot (y - x)\right)$$

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[4]   The proofs of all the numerical statements appearing in this paper are given in [9].

which is true for all $y \geqslant x \geqslant x^*$ because $V^*(x)$ is slowly varying. Summarizing we can say that n_{st} is a monotonously decreasing function switching from an essentially exponential decrease for $x < x^*$ to a power law for $x > x^*$.

C. How does Kelvin's statement that a droplet can be at most in a metastable equilibrium with a supersaturated vapour go together with Frenkel's statement that an ensemble of droplets can be thermodynamically stable?

To answer this question let us examine more closely the kinetic equations (5c) and (6a). We assume x to be so big that direct formation of droplets is negligible i.e.: $\dot{\phi}_x^{(2)} = 0$ in equation (5c). The quantity $c_x^{(1)} n_0 \, dt$ is the probability that a droplet A_x captures a A_1-molecule during the time dt; $e_{x-1}^{(1)} \, dt$ is the probability that one A_1-molecule evaporates from a droplet of size x in the time interval dt. $c_x^{(1)}$ does not depend very sensitively upon the droplet size x and we get from equation (A6) of Appendix A that

$$e_{x-1}^{(1)} = c_{x-1}^{(1)} n_0 \frac{\lambda_{x-1}}{\lambda_x} \cong c_x^{(1)} n_0 \frac{\lambda_{x-1}}{\lambda_x}.$$

A droplet of size x is more probable to decrease than to grow if the static distribution λ_x is decreasing and vice versa.

In the case of thermodynamic equilibrium at saturation or undersaturation ($a \leqslant 0$) is the static distribution λ_x monotonously decreasing (see equation (4)). Each cluster has the tendency to decrease but the total number $e_x^{(1)} \lambda_{x+1}$ of clusters passing per second from the size $x+1$ to size x equals the number $c_x^{(1)} n_0 \lambda_x$ growing from x to $x+1$ because there are correspondingly more clusters of size x than of size $x+1$. The total number of x-clusters per unit volume stays constant at λ_x in the thermodynamic limit. Nevertheless, each particular cluster changes its nature rather frequently and most probably disappears. This reveals the dynamical nature of thermodynamic equilibrium and stability.

In the case of the stationary distribution (11) at constant supersaturation ($a > 0$), Kelvins critical droplet size x^* disjoins two different regions of droplet sizes. The situation for the undercritical clusters is very similar to the equilibrium case just discussed. Each undercritical droplet is more probable to decrease than to grow but the stationary distribution $n_{st}(x, a)$ is a so strongly decreasing function of x that there is a constant excess rate $I(a)$ of growing droplets at each stage x of the chain of chemical reactions. The situation differs for the overcritical clusters. Each overcritical droplet is more probable to grow than to decay and a slow decrease of the stationary distribution is enough to produce the excess rate I.

D. Let us now discuss the excess rate $I(a) = \dot{\phi}_x^{(1)}$ in more detail. Equation (5a) shows that $\dot{\phi}_x^{(1)}$ is the net flow of vapour molecules A_1 to the droplets A_x caused by the reaction $A_1 + A_x \leftrightarrow A_{x+1}$. The quantity $\dot{\phi}_x^{(1)}$ depends on n_x and n_{x+1} and – as the discussion in the foregoing Part C reveals – can't be properly understood by a physical picture focussing attention on a single droplet. The problem of condensation by nucleation would, nevertheless, much simplified – conceptually as well as mathematically – if we could interpret $\dot{\phi}_x^{(1)}/n_x$ as mean condensation rate on the droplet of size x. Or in other words: if we could replace equation (6a) by

$$\dot{\phi}_x^{(1)} = (c_x^{(1)} n_0 - e_{x-1}^{(1)}) \cdot n_x. \tag{17}$$

The quantity

$$\nu(x, a) = c_x^{(1)} n_0 - e_{x-1}^{(1)} = D(x) \frac{\partial}{\partial x} \ln \lambda(x, a) \tag{18}$$

is the mean condensation rate on a droplet of size x.

Equations (16) show that formula (17) and the corresponding physical interpretation (a single droplet picture!) are valid for stationary overcritical droplets but *not* for undercritical ones.[5])

It is interesting to discuss the same connection in the language of thermodynamics. For this purpose, we write the quantity $\dot{\phi}_x^{(1)}/n_x$ as follows:

$$\dot{\phi}_x^{(1)}/n_x = D(x) \frac{\partial}{\partial x} \ln \frac{\lambda(x)}{n(x)} = \frac{D(x)}{kT} \left\{ \mu - \left(\frac{\partial G_x}{\partial x} + kT \frac{\partial}{\partial x} \ln N_x \right) \right\} \tag{19}$$

(we have used equation (3)). Equation (19) is valid for an arbitrary droplet distribution N_x. It shows the physical significance of the function $D(x)$: $D(x)/kT$ is the proportionality factor between the net flow $\dot{\phi}_x^{(1)}/n_x$ of vapour to the droplets A_x and the difference between the chemical potentials per water molecule of the vapour (μ) and of the liquid in the droplet. The latter consists of two terms: $\partial_x G_x$ would be the chemical potential in the droplet of size x if only this single droplet is in the atmosphere. But one has in general a whole droplet spectrum $n(x)$ causing mixing terms in the thermodynamic potentials of the fog. If a water molecule is removed from a droplet, the other droplets not being touched, the droplet spectrum n is changed. This yields the second statistical term.

Equation (16c) indicates that this statistical term can be neglected for droplets clearly bigger than Kelvin's critical size x^*. But it is crucial for smaller droplets: $\mu - \partial_x G_x < 0$ for droplets smaller than the critical ones whereas I/n_{st} is always positive.

We can, therefore, not agree with the usual 'critical fluctuation' picture of nucleation focussing attention on a single droplet: 'When a vapor condenses into liquid droplets, the first stage is the formation of nuclei. When the size of a nucleus is smaller than the critical size, it is not stable and grows by fluctuation; it becomes stable and goes into the growth stage only after it passes through the critical size'. ([5], page 67).

We have already mentioned that the thermodynamic stability of the droplet species A_x is not in contradiction to the fact that each particular droplet most probably decays. We stress, moreover, that the equations (5) and (6) – and consequently equation (7) too – are deterministic equations for the time evolution of the mean values of the droplet number. They do not describe any fluctuations and they treat all clusters – overcritical and undercritical ones – on an equal footing. We see no justification to call the growth of undercritical droplets a 'growth by fluctuation'.

III. A quasi-stationary model of condensation

It is, unfortunately, very difficult to obtain solutions of the kinetic equation (7) if the supersaturation varies in time or to account for the decrease of

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[5])   This point is incorrectly discussed in [8], p. 308.

supersaturation by condensation. The discussions in paper [8] are, thus, somehow disconnected from experience. In order to obtain a more realistic description of a closed supersaturated system, we must further simplify our theoretical approach. We may use the discussion of the preceding chapter as building blocks for such a simplification.

We first remark that the actual droplet distribution $n(x, t)$ must be close to the stationary distribution $n_{st}(x, a)$ only in an interval $[2, x_0)$ with $x_0 \geqslant 2x^*$ in order to assure the stationary value $I(a)$ of the current $\dot{\phi}_x^{(1)}$. The longest relaxation times for this process are of the order of $1/D(x^*)$ ([10], Appendix B and [8], Chapter II.3) which is about 3×10^{-8} sec for the system water–air.

The time lag needed to attain the stationary distribution may be neglected if the supersaturation parameter $a(t)$ varies so slowly that $|\dot{a}(t)/a(t)| \ll D(x^*)$. We have then always the stationary distribution $n_{st}(x, a(t))$ given by equation (11) in the interval $[2, x_0)$ and the droplet flow $I(a(t))$ at x_0: The quantity $I(a(t))$ can be considered as nucleation rate for the interval $[x_0, \infty)$ of the droplet spectrum.

As far as now the droplet distribution in the interval $[x_0, \infty)$ is concerned, the discussion in the foregoing chapter suggests that it can be described by a condensation rate

$$v(x, a) = D(x) \frac{\partial}{\partial x} \ln \lambda(x, a) = D(x) \cdot (a - bx^{-1/3}) \tag{20}$$

on each droplet.

Formula (20) is obtained from equation (19) by neglecting the statistical term $\partial_x \ln n$ against $\partial_x \ln \lambda$. We introduce, therefore, the following *criterion of quasi-stationarity*:

$$\left| \frac{\partial}{\partial x} \ln n(x, t) \right| \ll \left| \frac{\partial}{\partial x} \ln \lambda(x, a(t)) \right| \tag{21a}$$

and

$$\left| \frac{d}{dt} \ln a(t) \right| \ll D(x^*(t)) \tag{21b}$$

for all times t.

Replacing the function $\dot{\phi}_x^{(1)}/n_x$ given by formula (19) by the function v transforms the diffusion-type differential equation $\partial_t n = \partial_x (D\lambda \, \partial_x (n/\lambda))$ valid for the interval $[x_0, \infty)$ into a linear *first order* partial differential equation for the droplet distribution $n(x, t)$:

$$\frac{\partial n}{\partial t} + v \frac{\partial n}{\partial x} = -n \frac{\partial v}{\partial x}. \tag{22}$$

Its solution can be visualized as a differentiable two-dimensional surface in the (t, x, n)-space containing the curve

$$\{\tau, x_0, I(a(\tau))/v(x_0, a(\tau)) = n_0(\tau)\} \tag{23}$$

(the initial conditions. We assume x_0 to be constant and of the order of $2x^*(t)$. It is not important to specify x_0 more precisely).

This solution of the differential equation (22) can be analytically described using its characteristic curves. A characteristic curve is a solution of the following

set of ordinary differential equations:

$$\frac{dt}{ds} = 1 \tag{24a}$$

$$\frac{dx}{ds} = v \tag{24b}$$

$$\frac{dn}{ds} = -n \frac{\partial v}{\partial x} \tag{24c}$$

where s is the parameter of the curve. Each solution of the partial differential equation (22) can be produced by a one parameter set of characteristic curves:

$$\{(t(s, \tau), x(s, \tau), n(s, \tau))\}$$

(see [11] for mathematical details).

One has a certain freedom in choosing the parameters s and τ. First of all does s not appear explicitly in the equations (24). We can, thus, set $s = t$ without loss of generality. We, secondly, choose τ to be the creation time of the droplet. The equation (24b) reads then as

$$\left. \frac{\partial x}{\partial t} \right|_\tau = v(x(t, \tau), a(t)) \tag{25}$$

with the initial condition

$$x(\tau, \tau) = x_0 \tag{26}$$

from (23). The differential equation (25) is nothing else than the equation of growth for a droplet created at time τ; v is indeed the condensation rate.

Equation (24c) becomes

$$\frac{\partial \ln n}{\partial t} = -\frac{\partial v}{\partial x} \tag{27}$$

determing n up to an arbitrary factor of τ which is specified by the second initial condition $n(\tau, \tau) = n_0(\tau)$. It is possible to calculate the function $n(t, \tau)$: We conclude from equations (25) and (26) that

$$\left. \frac{\partial}{\partial t} \left(\ln \left| \frac{\partial x}{\partial \tau} \right| \right) \right|_\tau = \frac{\partial v}{\partial x}, \qquad \frac{\partial x}{\partial \tau}(\tau, \tau) = -v(x_0, a(\tau))$$

and together with (27) that the flow conserves the quantity $|\partial x / \partial \tau| \cdot n$. It follows that

$$n(t, \tau) = I(a(\tau)) \left| \frac{\partial x}{\partial \tau} \right|^{-1}. \tag{28}$$

The problem to find the solution of the partial differential equation (22) is reduced to the integration of the ordinary first order differential equation (25).

This solution of the partial differential equation may be visualized as indicated in Fig. 2: The droplets created at x_0 during the time interval $[\tau, \tau + d\tau]$ flow between the characteristic curves $\{t, x(t, \tau), n(t, \tau)\}$ and $\{t, x(t, \tau + d\tau), n(t, \tau + d\tau)\}$
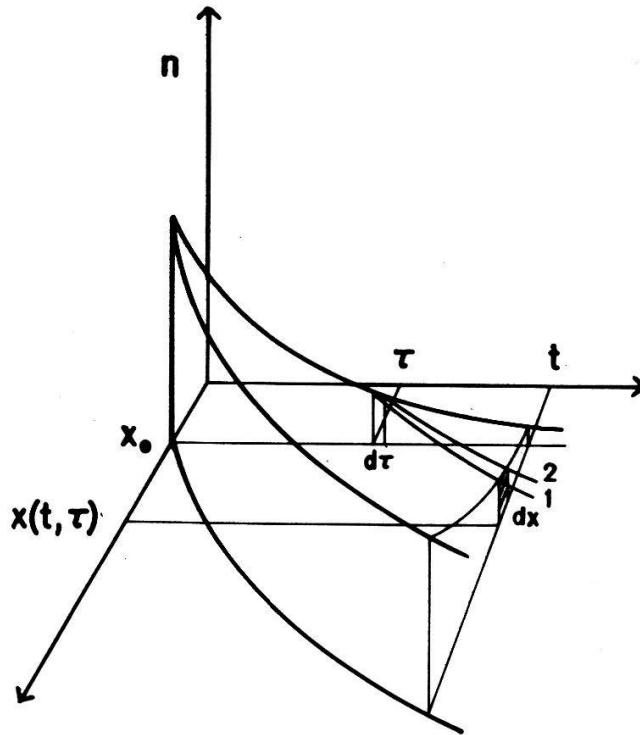
Figure 2
Geometric visualization of the quasistationary solution: The hatched area equals the distance $(dx)(t, \tau)$ between the x-components of the infinitesimally neighbouring characteristic curves 1 and 2 times their n-component $n(t, \tau)$. It doesn't depend upon time.

in the (t, x, n)-space with the velocity given by equations (25) and (26). The function $n(t, \tau)$ is inversely proportional to the distance $dx = |\partial x/\partial \tau| \, d\tau$ between the two infinitesimally close characteristics because the flow conserves the number of droplets.

IV. The decay of supersaturation in an isothermic and isobaric two components system

A. The approximation of quasistationarity considerably reduces the mathematical complexity of the condensation problem: Suppose we know the function $a(t)$. We have then to integrate the ordinary first order differential equation (25) instead of the second order partial differential equation (7). It remains the task to determine the decay of the supersaturation parameter $a(t)$ through condensation. To calculate this function we must specify the process conditions.

Let us consider the following system: The atmosphere shall consist of vapour and of an inert component B ('air'), the particle density n_v of the vapour being much less than the density n_B of the air. Temperature and pressure are held constant during the process of condensation. In this osmotic limit ($n_v \ll n_B$) is the supersaturation parameter given by the simple equation

$$a = \ln \frac{n_v}{n_s} \tag{29}$$

(see [6], Appendix B.2) where $n_s(T, p, n_B)$ is the saturation density of the vapour.

The number of water molecules per unit volume condensed in the droplets at time t is given by the integral:

$$\int_{x_0}^{\infty} dx\, n(x, t) \cdot x = \int_0^t d\tau\, I(a(\tau)) \cdot x(t, \tau).$$

We neglect the water contained in the droplets smaller than x_0 which is of the order of $2\lambda(2, a(t)) \ll n_0$. This is in accord with the fact that we have neglected the collisions $A_2 + A_2 \leftrightarrow A_4$.

The total amount of water shall not change during condensation. We get, thus, the following equation of motion for the supersaturation parameter $a(t)$:

$$e^{a(t)} = e^{a(0)} - \frac{1}{n_s} \int_0^t d\tau\, I(a(\tau)) \cdot x(t, \tau). \tag{30}$$

The equations (25), (26) and (30) form a closed set.[6] We remark that they contain only one free parameter: V^*.

One may object considering an isothermic process. The temperature of an adiabatically closed supersaturated atmosphere can change considerably by the produced heat of condensation – and heat diffusion is slow. We propose, nevertheless, to study the isothermic system.

It yields the most simple set of process conditions. To account for the temperature dependence of the parameters b, E, n_s, x_c increases much the complexity of the model without introducing new qualitative features. It further describes correctly the beginning of the condensation process and – as we will show – the stage of droplet formation.

B. We have computed the system of equations (25), (26) and (30) on a NORD-10 machine. The details of the numerical work are given in [9].[7]

Typical results are plotted in Fig. 3. The curves figure the supersaturation parameter a, an analytically calculable lower bound a_l of a we will discuss in Chapter V and the nucleation rate I as functions of time and in units of their initial values. Figure 3a represents a low initial supersaturation ($a_0 = 1.6$), Fig. 3c a high value ($a_0 = 1.9$).

Figures 3 look similar if we disregard the different time scales. Their most striking common feature is the fast decay of the nucleation rate and the symmetry

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[6]   After completion of a first version of the present work we get knowledge of a paper of Binder and Stauffer [10] dealing – among many other topics – also with the kinetics of droplet growth ([10], p. 381). They are interested in nucleation and condensation near the critical temperature of the system and use an equation similar to (35) together with the assumption of a constant nucleation rate to get an estimate of a 'condensation time'. We think that it is not adequate to consider a constant nucleation rate in discussing the decrease of supersaturation by homogeneous nucleation. On the contrary, it is the fact that the nucleation rate depends very sensitively upon supersaturation (see equation (15)) and varies, thus, strongly during the process of condensation which determines the kinetics of condensation.

[7]   We remark that for the numerical work we have neglected the factor $(1 - (x^*/x)^{1/3})$ in the function $\nu(x, a)$. This approximation has the great advantage that equation (25) can be integrated analytically by a separation of variables. It causes a relative error of the size x of the order $(x^*/x)^{1/3}$. The main contribution to the integral in equation (30) stems from the droplets $x(t, 0)$ created first. They are bigger than 10^{11} at time t_n when the decrease of $a(t)$ begins to influence the nucleation rate I (see Fig. 3 and Table 1). The relative error on the difference $a_0 - a(t)$ should then be smaller than 1‰.

Figure 3a,b,c

Numerical resolution of the equations (25) (30) and (35), (36) using the following values of the constants: $T = 261°K$, $p = 10^6 \, \mathrm{dyn \, cm^{-2}}$, $n_s = 6.80 \times 10^{16} \, \mathrm{cm^{-3}}$, $E = 2 \times 10^5 \, \mathrm{sec^{-1}}$, $b = 6.66$, $x_c = 10^{13}$, $V^* = 10^{-19} \, \mathrm{cm^3}$. The functions $a(t)/a_0$, $a_l(t)/a_0$, $I(a(t))/I_0$ are plotted for different initial values a_0. Note the different time scales! The hatched surface corresponds roughly to the number of droplets created after the nucleation time t_n (see Appendix C).
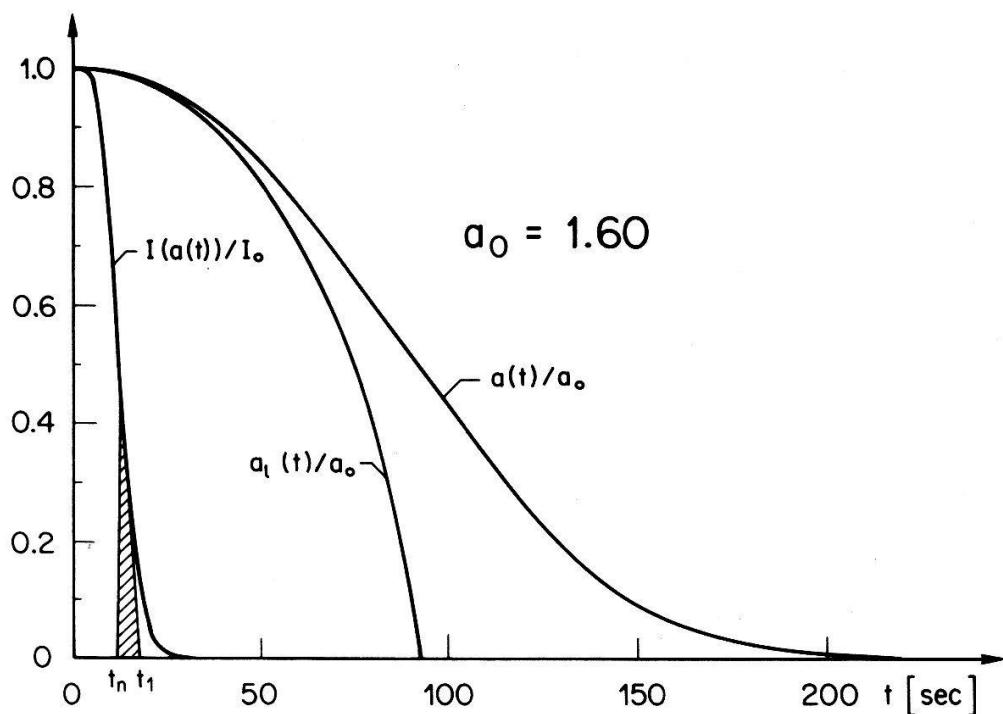

Figure 3a
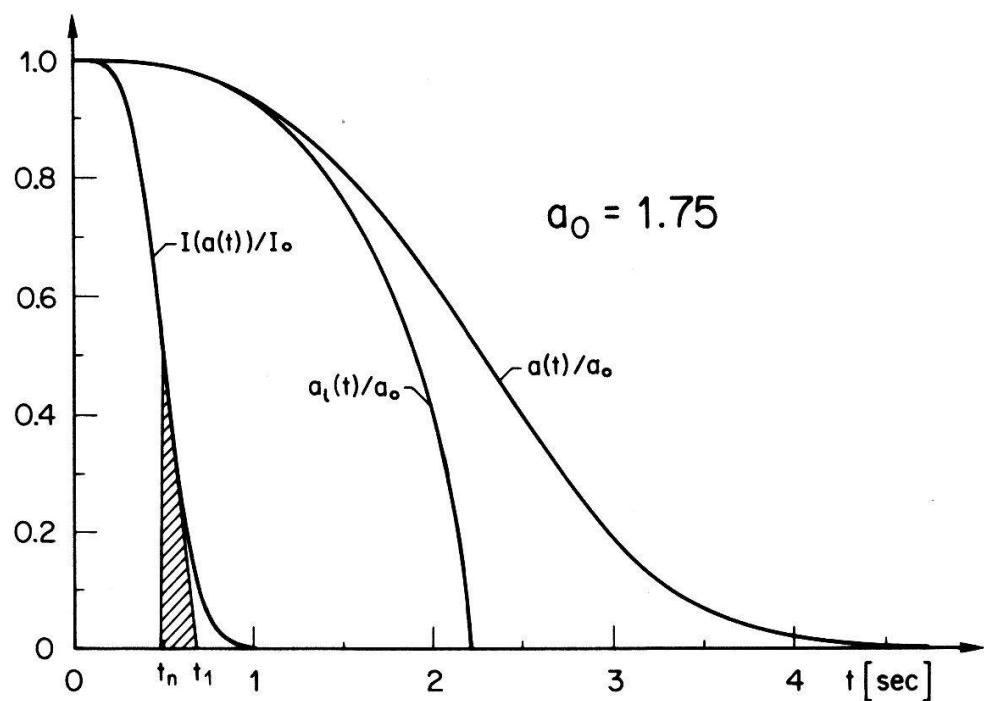
Figure 3b
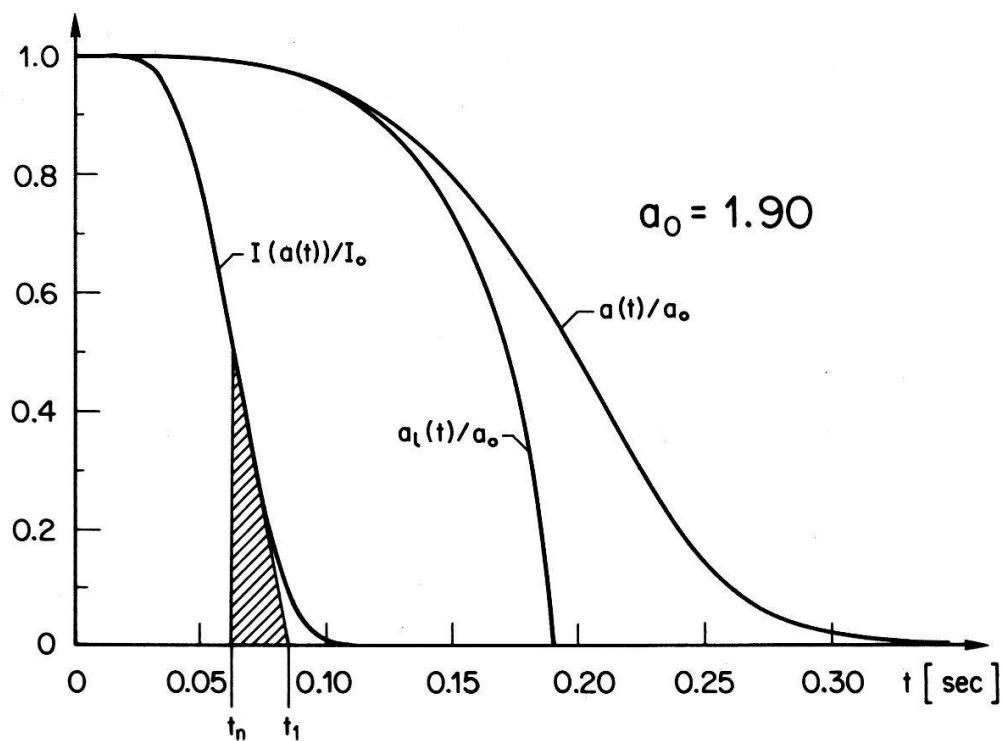
Figure 3c

of the curve $I(t)/I_0$ around the point $I(t)/I_0 = \frac{1}{2}$. We give an analytical argument for this symmetry in Appendix C.

This allows to introduce a *nucleation time* t_n by the following equation:

$$I(a(t_n)) = I_0/2 \qquad (31)$$

We expect that the total number of droplets per unit volume created during the condensation process is given by the product $I_0 t_n$ and that most of the droplets are created before the time t_n. This is confirmed by the numerical values of Table 1. The symbol $M(t)$ denotes there the number of droplets per cm³ created during the interval $[0, t]$.

V. The connection between the initial value of the nucleation rate and the total number of produced droplets

We derive in this chapter an explicit lower bound $a_l(t)$ of the supersaturation parameter. This bound is very close to $a(t)$ for times $t \leq t_n$ and can be used to get

Table 1

	Fig. 3a	Fig. 3b	Fig. 3c
a_0	1.60	1.75	1.90
$x_0^* = (b/a_0)^3$	72	55	43
$I_0 [\mathrm{cm}^{-3} \sec^{-1}]$	1.0×10^{-1}	1.35×10^3	2.0×10^6
$t_n [\sec]$	1.2×10^1	4.8×10^{-1}	6.2×10^{-2}
$M(t_n) [\mathrm{cm}^{-3}]$	1.0	5.6×10^2	1.1×10^5
$M(\infty) [\mathrm{cm}^{-3}]$	1.2	6.5×10^2	1.2×10^5
$I_0 t_n / M(\infty)$	0.961	0.992	1.009
$x(t_n, 0)$	7.8×10^{15}	2.7×10^{13}	2.4×10^{11}
$x(\infty, 0)$	2.5×10^{17}	6.4×10^{14}	5.0×10^{12}
$\bar{x} = n_s \cdot (e^{a_0} - 1)/(I_0 t_n)$	2.1×10^{17}	5.0×10^{14}	3.1×10^{12}

an analytical expression for the quantity $I_0 t_n$ close to the total number $M(\infty)$ of droplets per unit volume after condensation.

The foregoing discussion of the numerical results suggest to replace the nucleation rate $I(a(t))$ by the step function

$$I_{\text{step}}(t) = I_0 \cdot \theta(t - t_n). \tag{32}$$

Furthermore, equation (31) is equivalent to

$$a(t_n)/a_0 = \left(1 + \frac{2 \ln 2}{a_0 x_0^*}\right)^{-1/2} \simeq 1 - \frac{\ln 2}{a_0 x_0^*} \tag{33}$$

which is close to 1 because of the strong decrease of the nucleation rate $I(a)$ with a (see (15)). Thus,

$$\nu(x(t, \tau), a(t)) \simeq \nu(x(t, \tau), a_0), \tag{34}$$

at least for times $t_n \geq t \geq \tau \geq 0$. As we are interested in an explicit calculation of $M(\infty)$, we have to solve the system (25), (30) for $t \leq t_n$. In the approximation (32), (34) these equations become

$$\frac{\partial x_u}{\partial t}(t - \tau) = \nu(x_u(t - \tau), a_0) \tag{35}$$

with the initial condition $x_u(0) = 2x_0^*$ and

$$e^{a_l(t)} = e^{a_0} - \frac{1}{n_s} \int_0^t d\tau \, I_{\text{step}}(\tau) \cdot x_u(t - \tau). \tag{36}$$

The function $x_u(t - \tau)$ is an upper bound of $x(t, \tau)$; the function $a_l(t)$ is a lower bound of the supersaturation parameter $a(t)$ because I_{step} overestimates the number of big droplets and underestimates the number of small droplets.

We expect this bound to be very good for times $t \leq t_n$. This is justified by equation (33) and the fact that the main contribution to the integral in equation (36) stems from the smallest values of τ. The last argument also shows that the lower bound $a_l(t)$ deviates from $a(t)$ as soon as $a(t)/a_0$ deviates from 1 because $\nu(x, a)$ is roughly proportional to a and the approximation (34) for the condensation rate and consequently the approximation (35) for the function $x(t, 0)$ becomes then insufficient.

This is entirely confirmed by numerical computation [9]. We shall, therefore, in the following not distinguish between the values of t_n defined by $a(t)$ and by $a_l(t)$.

The functions $a_l(t)/a_0$ are plotted in Fig. 3. They are computed again within the approximation $\nu(x, a) = D(x) \cdot a$.

The great advantage of the system (35), (36) is that it can be analytically solved. It is, therefore, possible to give an explicit relation for t_n. With the abbreviations

$$z = x_u(t_n)^{1/3}, \qquad z_0^* = x_0^{*1/3}, \qquad z_c = x_c^{1/3},$$

the equations (35), (36) can be written (for $t = t_n$):

$$t_n = \frac{3}{Ea_0} \cdot z \cdot \left(\frac{1}{2}\frac{z}{z_c} + 1 + \frac{z_0^*}{z} \ln\left(\frac{z}{z_0^*} - 1\right)\right) + \frac{3}{Ea_0} 2^{1/3} z_0^* \times 0.070 \tag{37}$$

and

$$n_s \cdot (e^{a_0} - e^{a_1(t_n)}) = I_0 \cdot \frac{3}{Ea_0} \cdot z^4 \cdot \left(\frac{1}{5} \frac{z}{z_c} + \frac{1}{4} \right.$$

$$+ \sum_{n=1}^{3} \frac{1}{4-n} \left(\frac{z_0^*}{z} \right)^n + \left(\frac{z_0^*}{z} \right)^4 \cdot \ln \left(\frac{z}{z_0^*} - 1 \right) \bigg)$$

$$- I_0 \cdot \frac{3}{Ea_0} (2^{1/3} z_0^*)^4 \times 0.795. \qquad (38)$$

As in equation (13), we have here neglected the factor $1 + z_0^*/z_c$.

The left hand side of equation (38) is equal to $(\ln 2) \cdot n_s \cdot e^{a_0}/x_0^*$ (see equation (33)). Formula (38), is, thus, an implicit equation for z. By inserting this solution z into equation (37) we obtain an expression for $I_0 t_n$ as a function only of the initial values I_0/E, a_0. This expression can be made explicit in the following cases:

$$I_0 t_n = \frac{1}{2} \left(\frac{5 \ln 2 e^{a_0} n_s}{x_0^*} \right)^{2/5} \left(\frac{3}{a_0 z_c} \cdot \frac{I_0}{E} \right)^{3/5} \quad \text{for} \quad \frac{z_0^*}{z} \ll 1 \ll \frac{z}{z_c} \qquad (39)$$

$$I_0 t_n = \left(\frac{4 \ln 2 e^{a_0} n_s}{x_0^*} \right)^{1/4} \left(\frac{3}{a_0} \cdot \frac{I_0}{E} \right)^{3/4} \quad \text{for} \quad \frac{z_0^*}{z} \ll \frac{z}{z_c} \ll 1. \qquad (40)$$

These equations connect the initial nucleation rate I_0, which is difficult to observe, with $I_0 \cdot t_n$ the total number of droplets after condensation which is more easily measurable. Or, they can be used to determine the phenomenological
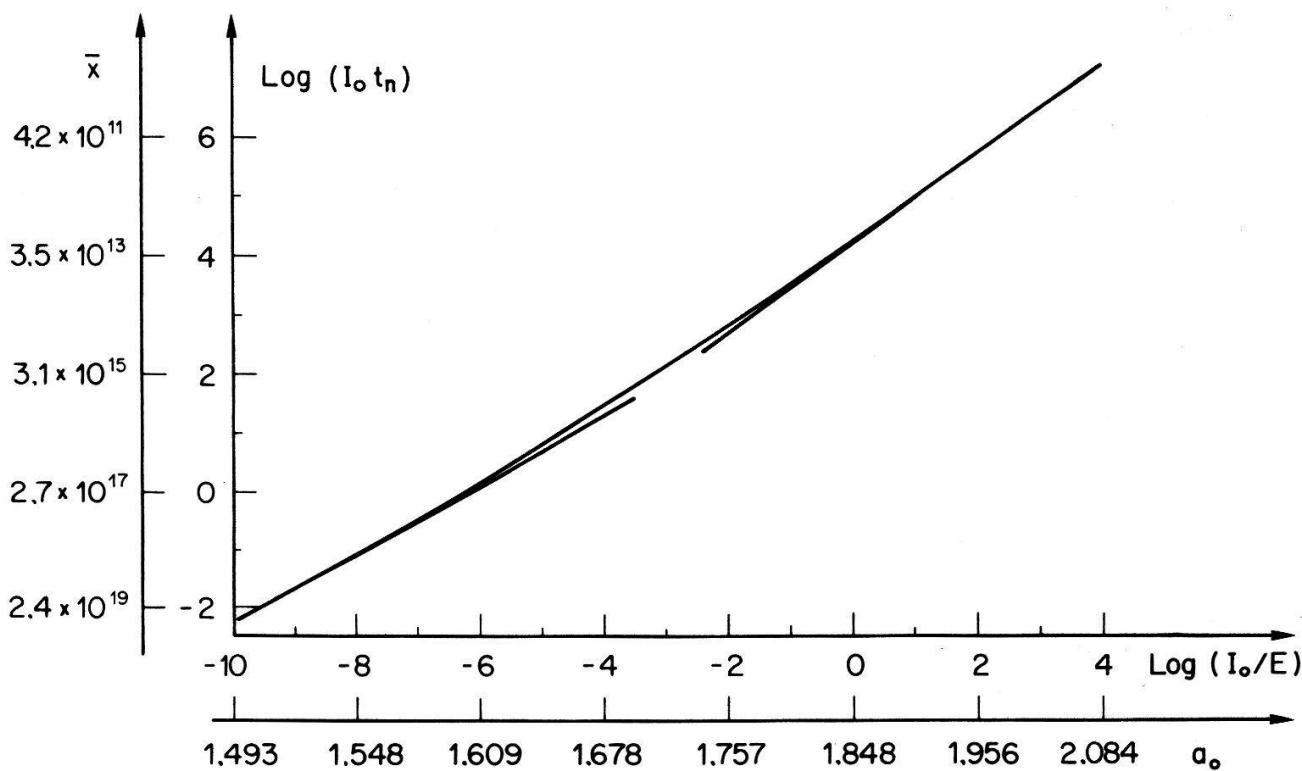

Figure 4

A plot of $\text{Log}(I_0 t_n)$ against $\text{Log}(I_0/E)$ for the values $n_s = 6.80 \times 10^{16} \text{ cm}^{-3}$, $b = 6.66$, $x_c = 10^{13}$, $E = 2 \times 10^5 \text{ sec}^{-1}$, $V^* = 10^{-19} \text{ cm}^3$. The corresponding values of the initial supersaturation a_0 and of the mean size of the droplets after condensation $\bar{x} = n_s(e^{a_0} - 1)/I_0 t_n$ are also indicated. The interrupted line indicates the approximations (39) and (40).

parameter V^*. We remark that only the quotient $I_0/E = (b/6\pi)^{1/2}\lambda(x_0^*, a_0)$ (see equation (13)) appears which does not depend upon the badly known absorption probability w (see Appendix B).

In Fig. 4, we have plotted the values of Log $(I_0 t_n)$ against Log (I_0/E). We also give the corresponding values of the initial supersaturation and of the mean size $\bar{x} = n_s(e^{a_0} - 1)/I_0 t_n$ of the droplets after condensation. High initial supersaturation produces a dense and fine fog, low initial supersaturation comparatively few but big droplets.

The nucleation time t_n is roughly proportional to I_0^{-c} with $0.25 \le c \le 0.4$ depending on the value of I_0. The dependence of t_n upon supersaturation is, therefore, weaker than one would expect from a consideration of the nucleation rate alone suggesting a nucleation time proportional to I_0^{-1}.

Appendix A

Consider a mixture of substances $A_1, A_2, \ldots, A_z$ in which R chemical reactions take place:

$$\sum_{j=1}^{z} a_j^r A_j \leftrightarrow \sum_{j=1}^{z} b_j^r A_j, \qquad r = 1, 2, \ldots, R. \tag{A.1}$$
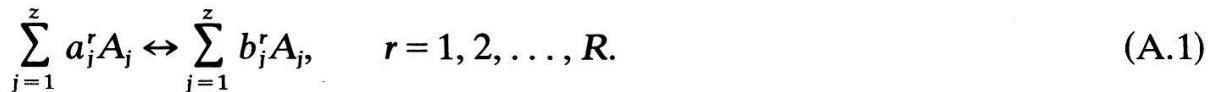
The reaction coefficients a_j^r, b_j^r are positive integers or zero. The state of the rth reaction is indicated by the reaction parameter ϕ^r. The number density n_j of the substance A_j is given by

$$n_j = n_j(0) + \sum_{r=1}^{R} (b_j^r - a_j^r)\phi^r. \tag{A.2}$$

The reaction parameters ϕ^r are now the independent particle number variables of the system. The differential df of the Helmholtz free energy per volume unit equals

$$df = -s\,dT + \sum_{j,r}^{z,R} (b_j^r - a_j^r)\mu_j\,d\phi^r. \tag{A.3}$$

In equilibrium, the activities

$$\alpha^r = \sum_{j=1}^{z} (b_j^r - a_j^r)\mu_j \tag{A.4}$$

are zero.

An elementary probability consideration yields the following expression for the time derivative $\dot{\phi}^r$

$$\dot{\phi}^r = c^r(T, n_0) \cdot \prod_{j=1}^{z} n_j^{a_{j^r}} - e^r(T, n_0) \cdot \prod_{j=1}^{z} n_j^{b_{j^r}} \tag{A.5}$$

if we assume that the substances $A_1, \ldots, A_z$ form a dilute solution in some chemical inert solvent A_0 (or an ideal mixture of ideal gases).

Let us call a set of number densities $\bar{n}_1, \bar{n}_2, \ldots, \bar{n}_z$ *static* if the corresponding

$\dot{\phi}^r = 0.$[8]) This implies:

$$c^r \prod_{j=1}^{z} \bar{n}_j^{a_j^r} = e^r \prod_{j=1}^{z} \bar{n}_j^{b_j^r} \equiv L^r, \qquad r = 1, 2, \ldots, R. \tag{A.6}$$

In the neighbourhood of a static state $(n_j = \bar{n}_j + \delta n_j)$ is

$$\dot{\phi}^r = L^r \sum_{j=1}^{z} (a_j^r - b_j^r) \frac{\delta n_j}{\bar{n}_j}. \tag{A.7}$$

This is equivalent to

$$\dot{\phi}^r = -\frac{L^r}{kT} \alpha^r \tag{A.8}$$

if we assume that the activities α^r are zero for a static state of the system

$$\alpha^r(T, n_0, \bar{n}_1, \bar{n}_2, \ldots, \bar{n}_z) = 0 \tag{A.9}$$

because

$$\mu_j = \varphi_j(T, n_0) + kT \ln n_j$$

in the osmotic limit $(n_j \ll n_0)$. Equation (A.8) is a special case of a general principle of the thermodynamics of irreversible processes, namely that the 'currents' $\dot{\phi}^r$ are linear combinations of the corresponding 'entropy conjugated potentials' $\alpha^r/(kT)$:

$$\dot{\phi}^r = -\sum_{s=1}^{R} \frac{L^{rs}}{kT} \alpha^s.$$

The matrix L^{rs} is positive and symmetric (Onsager's relations) [12]. In our case is L^{rs} diagonal.

The equations (A.9) are clearly true for equilibrium. We *assume* that they are true also for static states out of equilibrium. The functions $\alpha^r(T, n_0, \bar{n}_1, \ldots, \bar{n}_z)$ are then defined as analytic continuations of the equilibrium functions. The equations (A.9) together with the initial conditions (A.2) determine, in general, the static values $\bar{n}_1, \bar{n}_2, \ldots, \bar{n}_z$ uniquely. The quotient e^r/c^r is, therefore, given by the thermodynamic equilibrium properties of the system.

Appendix B

We calculated the numerical values of the constants b, E, x_c for the system water – air at the pressure $p = 10^6$ dyn cm^{-2} and for the temperatures 261°K, 300°K. The numerical values of the involved physical constants are taken from Landolt–Börnstein, Zahlenwerte und Funktionen ..., 6. Auflage, Springerverlag, Berlin. These values are known up to 1‰ except the absorption probability w which is not well known but clearly much smaller than 1. We have chosen $w = 0.04$. The quantity E is proportional to w, x_c is proportional to w^{-3}. The function $D(x)$ becomes, thus, independent on w for $x^{1/3} > x_c^{1/3}$.

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[8])   Our static state corresponds to the balanced steady state of Ref. [15].

T	261°K	300°K
b	6.663	5.374
E	$1.8 \times 10^5 \, \text{sec}^{-1}$	$2.4 \times 10^6 \, \text{sec}^{-1}$
x_c	6×10^{12}	9×10^{12}

The increase of the quantity E with temperature is due to the increase of the vapour saturation density n_s.

Appendix C

We derive an analytical argument for the symmetry of the function $I(a(t))/I_0$ around the point $I(a(t_n))/I_0 = \frac{1}{2}$ using the explicit lower bound $a_l(t)$ (see equations (37), (38)). As we are interested in times t such that $a_0 - a_l(t) \ll 1$ but $(x_u(t)/x_0^*)^{1/3} \gg 1$ these equations can be simplified to

$$t \sim \frac{q^2}{2} + q$$

$$a_0 - a_l(t) \sim \frac{q^5}{5} + \frac{q^4}{4}$$

with

$$q = (x_u(t)/x_c)^{1/3}.$$

The first coefficients of the Taylor series

$$I(a(t))/I_0 = \sum_{j=0}^{\infty} A_j \cdot (t - t_n)^j \qquad (C.1)$$

equal then

$$A_0 = \tfrac{1}{2}, \qquad A_1 = -\frac{5 \ln 2}{4 t_n} \left(1 + \frac{3}{4 q_n + 5} \right)$$

$$A_2 = A_1^2 \left(1 - \frac{3}{5 \ln 2} \left(1 + \frac{1}{4 q_n + 4} \right) - \frac{3 a_0^2}{b^3} \right)$$

where $q_n = q(t_n)$. We have used definition (13) of the function $I(a)$ and equation (33).

For times t such that $|A_1 \cdot (t - t_n)| \leq A_0$ we have

$$\left| \frac{A_2 \cdot (t - t_n)^2}{A_1 \cdot (t - t_n)} \right| \leq \frac{1}{2} \left| 1 - \frac{3}{5 \ln 2} \left(1 + \frac{1}{4 q_n + 4} \right) - \frac{3 a_0^2}{b^3} \right| < 0.06.$$

The second order term of the Taylor series (C.1) is, thus, dominated by the first order term in the time interval where the function $I(a(t))/I_0$ differs from 1 and from 0. This is the reason why, to a very good approximation, $I(a(t))$ is symmetric around t_n.

Finally, we estimate the fraction of droplets created after the nucleation time t_n using a linear approximation of the function I around t_n. This fraction Q is then

given by

$$Q = \frac{1}{I_0 t_n} I_0 \cdot \int_{t_n}^{t_1} (A_0 + A_1(t - t_n)) \, dt$$

$$= 1 \bigg/ \left(10 \ln 2 \left(1 + \frac{3}{4q_n + 5}\right)\right) = \begin{cases} 0.09 & \text{if} \quad q_n \ll 1 \\ 0.14 & \text{if} \quad q_n \gg 1. \end{cases}$$

The time t_1 is given by the equation $A_0 + A_1 \cdot (t_1 - t_n) = 0$ (see Fig. 3). Numerical calculation confirm this simple estimate (see Table 1).

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