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On the formation of droplets in supersaturated systems

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Abstract. The formation of droplets in a supersaturated vapor is described by a set of chemical reactions. The reaction kinetics are treated in the framework of the thermodynamics of irreversible processes. We emphasize the difference between homogeneous nucleation (the formation of pure droplets from supersaturated vapor) and heterogeneous nucleation (dirt nuclei collect water and grow) because different sets of chemical reactions are involved. We first derive the kinetic equation for heterogeneous nucleation which is identical with the equation of Zeldovich and Frenkel [6], [4] usually accepted for homogeneous nucleation. The kinetic equation, together with suitable boundary conditions, form a well defined initial value problem which we discuss for constant undersaturation or saturation and for constant supersaturation of the vapor. The time evolutions for some simplified models are calculated explicitly. In the second part of the paper, homogeneous nucleation is discussed. We derive the kinetic equation for homogeneous nucleation, and starting from it, an integral equation for the nucleation rate which we solve for a simple but realistic model. We then determine the stationary nucleation rate of the kinetic equation. Our result contains the Becker-Döring nucleation rate [3] as a special case.

I. Introduction

The theory of nucleation is not a very old science. The pioneering work of Volmer and Weber [1] dates back to 1926. They measured the nucleation rate (the number of droplets formed per second in a supersaturated vapor) and observed a characteristic behaviour: no nucleation occurs if the supersaturation stays below a critical value, above this threshold nucleation becomes very strong. Volmer explains this in the following way. The amount of Gibbs free energy necessary to form a droplet from the supersaturated vapor has a maximum at Kelvin's critical radius r_K (A derivation may be found in textbooks of thermodynamics. See f.i. [2]). This means that a droplet of radius r_K is metastable. Smaller droplets decay, bigger droplets grow. The nucleation-rate is determined by the frequency of density fluctuations generating droplets of overcritical size.

I do not find Volmer's theoretical explanation satisfying. His rather qualitative considerations determine the nucleation rate only to within a factor which is difficult to estimate. But the main objection is that density fluctuation in a pure phase and (local) phase transitions are two different things which should be kept apart. I do not think that droplets are formed by density fluctuations (see Section III.5 for a detailed discussion).

A more satisfying nucleation theory was proposed by Becker and Döring [3]. They considered that droplet formation is governed by a set of coupled reaction rate equations for evaporation and condensation on the droplet, and they evaluated

the solution for a particular stationary process. I think that their result is correct in principle, but the derivation must be criticized. The authors treated only a very special problem with methods which seem to be chosen *ad hoc*. The significance and the consequences of their assumptions are, therefore, not clear. The connection between their stationary process and real nucleation experiments is not at all obvious. The derivation of the nucleation formula is obscured by the fact that some results of an equilibrium theory are used but no consistent thermodynamics of fog is developed. Their thermodynamic considerations are, in fact, wrong. The vapor pressure of a droplet in fog depends not only upon the radius of the droplet but also on the number of droplets of a given size (see equation (II.5)). However, this causes only a minor influence on the final result.

Lord Kelvin's statement that a droplet can never be in equilibrium with the vapor inhibited the development of an equilibrium theory of fog for more than 60 years. Fog was considered as caused uniquely by the presence of dirt nuclei. It was J. Frenkel [4] who remarked that nevertheless an ensemble of droplets could be thermodynamically stable and that 'even in the range of thermodynamic stability of the phase A, the latter is not strictly homogeneous, but contains embryos of a second phase B (in the form of liquid drops, gas bubbles, small crystals, etc.)...' ([4], p. 382).

Frenkel's thermodynamics of fog are based on the following ideas. A liquid droplet containing j molecules of the gaseous phase A_1 is itself considered as a molecule of a new substance A_j and fog as a mixture of all these substances. Condensation and evaporation on the droplets are described by a set of chemical reactions between the different substances A_j ($j \geqslant 1$). The conditions of chemical equilibrium yield the concentration of the droplets of a given size. They turn out to be bigger than zero (but very small in practice); fog is stabilized by the mixing entropy. Frenkel's thermodynamics of fog is critically revised and extended in Reference [5].

Frenkel does not go beyond Becker and Döring's work as far as nucleation theory is concerned. Starting from the same set of equations, he derives a differential equation for the time development of the number of droplets which was found independently also by J. Zeldovich (Reference [4], p. 393 and [6]). Frenkel and Zeldovich reproduce Becker and Döring's nucleation formula by considering a stationary solution of the mentioned differential equation on which they impose particular boundary conditions. They do not justify the special choice they make. It is shown in this paper that a justification is in fact impossible because they started from a wrong equation.

Becker–Döring and Frenkel–Zeldovich based their nucleation theory upon a kinetic theory of condensation on a single droplet. We propose in this paper a different scheme, namely, to take seriously Frenkel's idea to consider fog as a mixture of different chemical substances in which chemical reactions take place. In a previous paper [5] we discussed the thermodynamics of fog and found an expression for the Helmholtz free energy of fog. This allows to treat the kinetics of the chemical reactions describing the droplet formation in the framework of the thermodynamics of irreversible processes.

This phenomenological approach provides some advantages compared with the purely kinetic treatment mentioned above. In a phenomenological theory the assumptions and restrictions are formulated in a language near experiment and the theory itself has a simple structure. The general form of the equations can be gained very easily. It is true, though, that only a kinetic theory can predict the numerical

values of the proportionality coefficients which occur. We determine them consequently by comparing the phenomenological with a kinetic treatment.

In the phenomenlogical approach it becomes clear how one has to account for the two different types of chemical reactions which mainly occur in fog: (i) Growth of the droplets by successive accumulation of vapor molecules; (ii) Instantaneous formation of a droplet out of the vapor. The first set of reactions does not change the total number of droplets, it alone determines heterogeneous nucleation (i.e. how dirt nuclei collect water and grow). The second set of reactions produces droplets. Both types of chemical reactions contribute, therefore, to homogeneous nucleation (i.e. the formation of pure droplets from supersaturated vapor).

These considerations indicate that one should treat separately homogeneous and heterogeneous nucleation. The usual kinetic equation (II.7) of Zeldovich and Frenkel describes only heterogeneous nucleation. We shall have to find another equation for homogeneous nucleation.

In Section II, heterogeneous nucleation is discussed. We derive the kinetic equation (II.7) for heterogeneous nucleation together with the appropriate boundary conditions (II.15) for the distribution function of the droplet sizes. A modification occurs because we account for the fact that the condensed vapor has to be transported through the atmosphere. This effect becomes important for water droplet in air if the droplet radius exceeds 5.10^{-6} m.

The differential equation of Zeldovich and Frenkel and the indicated boundary conditions form a well defined initial value problem. In Section II.3, we discuss the time evolution of the spectrum of droplet sizes when the degree of saturation of the atmosphere is held fixed. In the case of saturation or undersaturation the droplet distribution converges towards its equilibrium value. For constant supersaturation the spectrum of droplet sizes falls to zero if time goes to infinity, but the total amount of water increases infinitely. The time development for some simplified models is explicitly calculated.

In section II.4, we establish a set of equations for the development in time of the mean value of the droplet size. These equations may be useful for numerical computations.

Homogeneous nucleation is discussed in Section III. We derive the kinetic equation (III.14) for homogeneous nucleation and starting from it, the integral equation (III.18) for the nucleation rate (Section III.2). We solve the nucleation equation (III.18) for a simple but realistic model.

In Section III.3, we determine the stationary nucleation rate of the kinetic equation (III.14). Our result contains the Becker–Döring nucleation rate [3] as a special case. The stationary nucleation rate is derived under the assumption that only the very smallest droplets are formed directly from the vapor and that all others grow by successive accumulation of single vapor molecules. This contradicts Volmer's statement that overcritical fluctuations should be responsible for nucleation. These questions are discussed more closely in Section III.5.

In Section III.4, we calculate the stationary nucleation rate for the droplet model given in Reference [5]. We compare the result with experiment and determine the constant V^* which was indetermined in the previous paper.

II. The kinetics of heterogeneous nucleation

II.1. The kinetic equation

In Reference [5] the following expression for the Helmholtz free energy F of fog was derived (see equation (III (3.2) in Reference [5]. For simplicity, we consider here only one kind and one size of dirt nucleus. Generalizations are evident):

$$F = F_0(T, V_0, N_0, N_B) + \sum_j f_j \left\{ F_j\left(V_0, T, V_j; \frac{N_0}{V_0}, \frac{N_B}{V_0}\right) + kT(\ln f_j - 1) \right\} \tag{II.1}$$

F_0 denotes the free energy of the atmosphere, V_0 its volume, N_0 the particle number of the water vapor, N_B the particle number of an inert gas, which eventually may be present in the atmosphere, f_j is the number of droplets containing j water molecules. F_j is the Helmholtz free energy of a droplet of size j in contact with the atmosphere and moving in the volume V_0, V_j denotes its volume. Explicit expressions for F_j are given in Reference [5].

The chemical potential $\mu_A^{(0)}$ of the water in the atmosphere is given by the equation

$$\mu_A^{(0)} = \left.\frac{\partial F}{\partial N_0}\right|_{f_j, N_B, T, V} = \mu_0 + \sum_j j \left.\frac{\partial F_j}{\partial N_0}\right|_{N_B, T, V} \tag{II.2a}$$

$$\mu_0 = \left.\frac{\partial F_0}{\partial N_0}\right|_{V_0, T, N_B} \tag{II.2b}$$

An expression for the chemical potential $\mu_A^{(j)}$ of the water in a droplet of size j can be obtained by the following consideration: if we add a molecule to a droplet of particle number j keeping fixed the number of water molecules in all other droplets, we change the number of droplets j from f_j to $f_j - 1$ and f_{j+1} to $f_{j+1} + 1$. The total volume

$$V = V_0 + \sum_j f_j V_j$$

of the system remains unchanged. Assuming that the system is always in mechanical equilibrium, we obtain

$$\mu_A^{(j)} = \pm \left(\frac{\partial F}{\partial f_{j\pm 1}} - \frac{\partial F}{\partial f_j} \right) \Bigg|_{N_0, N_B, V, T} = \frac{\partial}{\partial j} (G_j + kT \ln f_j) \tag{II.3}$$

where

$$G_j = F_j - V_j \frac{\partial F_j}{\partial V_j}$$

In equilibrium

$$\mu_A^{(0)} = \mu_A^{(j)}$$

and the droplet number f_j is proportional to λ_j defined as

$$\lambda_j \equiv \exp \frac{1}{kT} (j\mu_A^{(0)} - G_j) \tag{II.4}$$

We consider the difference $\mu_A^{(0)} - \mu_A^{(j)}$ as a 'driving force' which moves the distribution f_j toward the equilibrium value. The rate of condensation $\dot{n}_j$ on a droplet containing j molecules is given by

$$\dot{n}_j = - D_j \frac{\mu_A^{(j)} - \mu_A^{(0)}}{kT} = - D_j \frac{\partial}{\partial j} \ln \frac{f_j}{\lambda_j} \tag{II.5}$$

We derive an expression for the proportionality function D_j in the following section.

The droplet current I_j is defined as

$$I_j \equiv \dot{n}_j f_j = - D_j \lambda_j \frac{\partial}{\partial j} \left(\frac{f_j}{\lambda_j} \right) \tag{II.6}$$

We now consider the variable j as continuous.

Because the number of droplets is conserved, the continuity equation yields:

$$\frac{\partial}{\partial t} f(j, t) = - \frac{\partial}{\partial j} I(j) = \frac{\partial}{\partial j} \left(D(j) \lambda(j, t) \frac{\partial}{\partial j} \frac{f(j, t)}{\lambda(j, t)} \right) \tag{II.7}$$

This equation was derived by Frenkel [4] with purely kinetic arguments and under the assumption, that λ defined by (II.4) is a steady state solution. This assumption is clearly justified for systems below saturation. In the case of supersaturation $\lambda(j)$ corresponds to an infinite number of droplets per unit volume, which requires justification. In our approach $\lambda(j, t)$ has not primarily the meaning of a steady state solution (It is a *result*, the f proportional to λ are stationary solutions of (II.7)) but it is a mere abbreviation. $\mu_A^{(j)}$, $\mu_A^{(0)}$ and consequently the λ may depend upon time. The degree of supersaturation will be lowered in general by the condensation of water on the droplets.

Equation (II.7) is usually proposed to describe homogeneous nucleation (see f.i. [7]). We propose it for heterogeneous nucleation. For its derivation, only processes are taken into consideration which conserve the number of droplets (see Section III.1 for a detailed discussion of this point).

II.2. The function $D(j)$

We obtain an expression for $D(j)$ by comparing the phenomenological description with a simple kinetic model [8] of condensation. We suppose the molecules of the liquid phase to be in a potential well of depth U_0 with respect to that of the gas molecules. The velocities of the molecules obey Boltzmann's law. We denote by v the component of the molecular velocity perpendicular to the surface separating the liquid and the gas which we assume to be plane.

Molecules in a surface layer of depth $|v|\, dt$ moving from the liquid toward the gas with a kinetic energy exceeding U_0 can escape into the gas with probability w_l during the time dt. The current $i_{l \to g}$ of particles from the liquid into the gas given by

$$i_{l \to g} = w_l n_l \sqrt{\frac{m}{2\pi k T}} \int_{mv^2/2 = U_0}^{\infty} dv\, v\, e^{-mv^2/2kT} = w_l n_l \sqrt{\frac{kT}{2\pi m}}\, e^{-U_0/kT}$$

The molecules of the gas moving toward the liquid are absorbed with probability w. The particle current $i_{g \to l}$ from the gas into the liquid equals

$$i_{g\to l} = wn_g \sqrt{\frac{m}{2\pi kT}} \int_0^\infty dvv\, e^{-mv^2/2kT} = wn_g \sqrt{\frac{kT}{2\pi m}}$$

n_l, n_g are the numbers of molecules per unit volume in the liquid and in the gas. The net current is

$$i = i_{g\to l} - i_{l\to g} = w \sqrt{\frac{kT}{2\pi m}} (n_g - n_g^S) \tag{II.8}$$

where

$$n_g^S = \frac{w_l}{w} n_l\, e^{-U_0/kT}$$

is the saturation density determined by the equation $i = 0$.

We now calculate the difference of the chemical potentials of the liquid and the gas for two cases:

(a) for pure vapor considered as an ideal gas. The saturation pressure $p^S(T)$ is defined by the equation

$$\mu_g(p^S, T) = \mu_l(p^S, T)$$

Developing μ_g around the saturation pressure, we get

$$\frac{1}{kT}(\mu_g - \mu_l) \cong \frac{1}{kT} \frac{\partial \mu_g}{\partial p}\bigg|_{p^S} (p - p^S) = \frac{n_g - n_g^S}{n_g^S}$$

(b) for a mixture of vapor with an inert gas B under the assumption that the density of the vapor n_g is much smaller than the density n_B of the inert component B. One can show that in this limit

$$\mu_g\left(p, T, \frac{n_g}{n_B}\right) = \phi(p, T) + kT\left(\ln \frac{n_g}{n_B} + 0\left(\left(\frac{n_g}{n_B}\right)^\varepsilon\right)\right)$$

with $\varepsilon > 0$ and ϕ a function of the pressure and the temperature only (see appendix B of Reference [5]).

Setting

$$\frac{1}{kT}(\mu_g - \mu_l) \cong \ln \frac{n_g}{n_g^S} \cong \frac{n_g - n_g^S}{n_g^S} \tag{II.9}$$

we find from equation (II.5, 8, 9) for a droplet of radius r that

$$D = 4\pi r^2 \chi \quad \text{with} \quad \chi = wn_g^S \sqrt{\frac{kT}{2\pi m}} \tag{II.10}$$

for $w = 1$, equation (II.10) is identical with Frenkel's result [9].

The current in the atmosphere is a diffusion current and the density n_g is different on the surface of the droplet and away from the surface. Assuming spherical symmetry, we obtain the stationary current

$$i = \frac{\dot{n}_j}{4\pi r^2} = \delta \frac{\partial n_g^{(r)}}{\partial r}$$

where δ denotes the coefficient of diffusion.

Integrating the last equation yields:

$$n_g(r) = n_g(\infty) - \frac{\dot{n}_j}{4\pi r\delta}$$

Equation (II.8) refers to the density $n_g(r)$ near the surface but equation (II.5) contains the chemical potential of the atmosphere, which is characterized by $\mu_g(n_g(\infty))$. We must calculate the condensation current $\dot{n}_j$ as a function of $n_g(\infty) - n_g^S$

$$\dot{n}_j = 4\pi r^2\chi\left(1 + \frac{r\chi}{\delta n_g^S}\right)^{-1} \frac{n_g(\infty) - n_g^S}{n_g^S}$$

and get from equations (II.5, 9)

$$D = 4\pi r^2\chi\left(1 + \frac{r}{r_{cr}}\right)^{-1} \tag{II.11a}$$

with

$$r_{cr} = \frac{\delta}{w}\sqrt{\frac{2\pi m}{kT}} \tag{II.11b}$$

and

$$j = \frac{4\pi}{3} r^3 n_l - j^* \tag{II.12}$$

The constant j^* accounts for the dry volume of the nucleus. If the radius r of the droplet is smaller than r_{cr} formula (II.11a) is identical with formula (II.10). The effects of diffusion become important for droplets bigger than r_{cr} and slow down their growth.

For water in air at $T = 300°$ K and $p = 10^6$ dyn cm^{-2} the above constants are: $w = 0{\cdot}04$ [10], $\delta = 0.26$ cm^2 sec^{-1} [11], $p^S = 3.7 \times 10^4$ dyn cm^{-2}, [12] which yield: $r_{cr} = 4.5 \times 10^{-4}$ cm, $\chi = 5.3 \times 10^{20}$ sec^{-1} cm^{-2}, and $D(r_{cr}) = 6.7 \times 10^{14}$ sec^{-1}.

It would be more realistic to include the effects of the heat produced by condensation. One must then allow the temperature $T(j, t)$ of a droplet of size j at the time t to be different from the temperature T of the atmosphere and $\lambda(j, t)$ would depend on time. The law of heat diffusion yields a second equation connecting $f(j, t)$ and $T(j, t)$ and one has to determine simultaneously f and T. This is a much more complicated task than to determine $f(j, t)$ alone from the kinetic equation (II.7) when $\lambda(j)$ is independent of time. We, therefore, consider first the simpler problem.

II.3. The time evolution of the droplet distribution f

We assume in this section that the function λ defined by formula (II.4) does not depend upon time. It is then convenient to write equation (II.7) in the variable

$$y(j, t) = \frac{f(j, t)}{\lambda(j)} \tag{II.13}$$

which yields the equation

$$\frac{\partial}{\partial t} y(j, t) = \frac{1}{\lambda(j)} \frac{\partial}{\partial j}\left(D(j)\lambda(j) \frac{\partial}{\partial j} y(j, t)\right) \tag{II.14}$$

How does a given initial distribution $y(j, 0)$ develop in time? We first remark that the initial value problem is not defined properly by equation (II.14) only. One has to specify the boundary conditions at $j = 0, j \to \infty$. Equation (II.7) shall conserve the total number of droplets. We require, therefore, that

$$\int_0^\infty dj \frac{\partial}{\partial t} f(j, t) = I(0) - I(\infty) = 0$$

We do not add dry condensation nuclei (i.e. $I(0) = 0$) and the natural boundary conditions become

$$\lim_{j \to \substack{0 \\ \infty}} D(j)\lambda(j) \frac{\partial}{\partial j} y(j, t) = 0 \tag{II.15}$$

We show in the Appendix A, that the distribution $y(j, t)$ achieves a constant equilibrium value different from zero if the system is saturated or undersaturated and that the distribution y goes to zero as t goes to infinity in the case of supersaturation. The initial value problem (II.14) with the boundary condition (II.15) can in general not be solved analytically. This is, however, possible for some especially simple forms of $\lambda(j)$. These functions nevertheless represent the typical shape of λ obtained from droplet models (see [5]) and can yield some useful information.

A. Saturation and undersaturation. The function λ has in this case a very narrow maximum at some droplet size j_0. Therefore we replace

$$\lambda(j) = e^{-\phi(j)} \tag{II.16}$$

by

$$\lambda(j_0) \exp\left(- \frac{1}{2} \frac{d^2\phi}{(dj)^2}\bigg|_{j_0} (j - j_0)^2 \right) \tag{II.17}$$

and the function $D(j)$ which varies slowly in comparison to λ by the constant $D(j_0)$. Equation (II.14) is then written as

$$\frac{\partial}{\partial \tau} y(x, \tau) = \frac{1}{2} e^{x^2} \frac{\partial}{\partial x} \left(e^{-x^2} \frac{\partial}{\partial x} y(x, \tau) \right) \tag{II.18a}$$

with

$$x = \sqrt{\frac{1}{2} \frac{d^2\phi}{(dj)^2}}\bigg|_{j_0} (j - j_0) \tag{II.18b}$$

and

$$\tau = D(j_0) \frac{d^2\phi}{(dj)^2}\bigg|_{j_0} t \tag{II.18c}$$

The ansatz

$$y_\omega = e^{-\omega\tau} e^{x^2/2} u_\omega(x)$$

yields

$$- \frac{d^2}{(dx)^2} u_\omega + x^2 u_\omega = (2\omega + 1) u_\omega$$

which has bounded solutions only for $\omega \in \{0, 1, 2, \ldots\}$. The longest relaxation time of the system is

$$t_1 = \left(D(j_0) \frac{d^2\phi}{(dj)^2}\bigg|_{j_0} \right)^{-1} \tag{II.19}$$

For fog around soluble nuclei $\phi(j)$ equals

$$\phi(j) = \alpha j + \gamma j^{2/3} - s \ln j \tag{II.20}$$

if $j \gg s$, s being the number of molecules or ions of the soluble dirt nucleus (see [5]). The symbol α represents the difference between the chemical potential of the liquid and the gaseous phase, measured in units kT. It is

$$\alpha = \frac{1}{kT}(\mu_l(p, T) - \mu_g(p, T)) \tag{II.21}$$

The degree of saturation is characterized by α. $\alpha > 0$ for undersaturation and $\alpha < 0$ for supersaturation. The effect of surface tension is included in γ, which is given by

$$\gamma = 3\left(\frac{4\pi}{3}\right)^{1/3} \frac{\sigma v_l^{2/3}}{kT} \tag{II.22}$$

where σ is the surface tension and v_l the volume per molecule in the liquid. We can neglect the constant j^* in (II.12), which is of the order of $s \ll j$.

$\gamma \simeq 8$ for water at 300° K which yields at saturation ($\alpha = 0$) and for $s = 1.6 \times 10^{10}$ (see Reference [5], Section III.3. This value of s corresponds to $j_0 = 1.6 \times 10^{14}$):

$$t_1 = 1.2 \times 10^3 \text{ sec} \tag{II.23}$$

B. Supersaturation. As already indicated, the distribution goes to zero in this case and one has, therefore, to pose slightly different questions. An interesting quantity is the time dependence of the total amount of water condensed in the droplets

$$\Lambda_1(t) \equiv \int_0^\infty dj\, j f(j, t) \tag{II.24}$$

An eigenfunction expansion is inefficacious, since all expansion coefficients decrease in time; whereas, we expect Λ_1 to grow. This means that the two integrations in

$$\Lambda_1(t) = \int_0^\infty dj\, j \int_0^\infty d\omega\, e^{-\omega t} c(\omega) f_\omega(j)$$

cannot be interchanged ($c(\omega)$ are the expansion coefficients of the initial condition $f(j, 0)$ with respect to the eigenfunctions $f_\omega(j)$ belonging to the eigenvalue ω of the operator A defined in Appendix A). One has to know the propagator of the initial value problem (II.7.15):

$$f(j, t) = \int_0^\infty dl\, K(j, l, t) f(l, 0) \tag{II.25}$$

The kernel K of the propagator is determined by the properties

$$\left[\frac{\partial}{\partial t} - \frac{\partial}{\partial j}\left(D\lambda \frac{\partial}{\partial j}\left(\frac{1}{\lambda}(\cdot)\right)\right)\right] K(j, l, t) = 0 \quad \forall l, t \geqslant 0 \tag{II.26a}$$

$$\lim_{t \downarrow 0} K(j, l, t) = \delta(j - l) \tag{II.26b}$$

$$\lim_{j \to \infty} D(j)\lambda(j) \frac{\partial}{\partial j}\left(\frac{K(j, l, t)}{\lambda(j)}\right) = 0 \quad \forall l, t \geqslant 0 \tag{II.26c}$$

The conservation of the total number of droplets implies

$$\int_0^\infty dj\, K(j, l, t) = 1 \quad \forall l > 0, t \geqslant 0 \tag{II.27}$$

The boundary conditions

$$\lim_{j \to 0} D\lambda \frac{\theta}{\partial j}\left(\frac{K}{\lambda}\right) = 0 \quad \text{and} \quad \lim_{j \to \infty} K(j, l, t) = 0 \tag{II.26d}$$

are equivalent to the conditions (II.26c) because the equations (II.25, 26a, 26b, 26d) determine the kernel uniquely (see Appendix B).

We also prove in Appendix B that

$$K(j, l, t) \geqslant 0 \qquad \forall j, l, t \geqslant 0 \tag{II.28}$$

under conditions which are specified there. The inequality (II.28) is valid for all kernels that we use in this paper.

For a supersaturated system $\lambda(j)$ has typically a very sharp minimum at some place j_0. We distinguish two cases: $j_0 \gg 0$ and $j_0 = 0$.

B1: $j_0 \gg 0$

We proceed as in A: We replace $D(j)$ by a constant D_0 and $\lambda(j)$ by

$$\lambda(j_0) \exp \tfrac{1}{2}a^2(j - j_0)^2 \quad a > 0 \tag{II.29}$$

Furthermore, we extend the range of j from $-\infty$ to $+\infty$. The kernel is then given by

$$K(x, z, \tau) = (\pi(e^{2\tau} - 1))^{-1/2} \exp - \frac{(x - z\, e^{\tau})^2}{e^{2\tau} - 1} \tag{II.30}$$

where the new variables are defined as

$$x = \frac{a}{\sqrt{2}}(j - j_0) \tag{II.31a}$$

$$z = \frac{a}{\sqrt{2}}(l - j_0) \tag{II.31b}$$

$$\tau = D_0 a^2 t \tag{II.31c}$$

Using the kernel (II.30), one can write equation (II.25) in the form

$$f(x, \tau) = e^{-\tau} \pi^{-1/2} \int_{-\infty}^{+\infty} dz\, e^{-z^2} f(z(1 - e^{-2\tau})^{1/2} + x\, e^{-\tau}, 0) \tag{II.32}$$

which clearly illustrates how the distribution flattens and spreads out.

We define Λ_n by

$$\Lambda_n = \int_0^\infty dj\, j^n f(j, t) \tag{II.33}$$

Equation (II.32) yields

$$\Lambda_1(t) - j_0\Lambda_0 = \Lambda_1(0) - j_0\Lambda_0) \exp(D_0 a^2 t) \tag{II.34}$$

The exponential growth of the water content of the droplets is not realistic as we shall show in Section II.4. The function $\lambda(j)$ is rather proportional to $\exp(-\alpha j)$ $(\alpha < 0)$ than to $\exp(a^2/2)j^2$ for $j \gg j_0$.

B2: $j_0 = 0$

We replace again $D(j)$ by a constant D_0 and $\lambda(j)$ by

$$\lambda(0)\, e^{aj} \tag{II.35}$$

This choice of D and λ leads to the kernel

$$K(\xi, \varphi, \tau) = (4\pi\tau)^{-1/2} \exp - \frac{(\tau - \xi + \varphi)^2}{4\tau} - \frac{\partial}{\partial \xi}\left\{ e^{\xi} (4\pi\tau)^{-1/2} \int_0^\infty dy \exp - \frac{(\tau + \xi + y + \varphi)^2}{4\tau} \right\} \tag{II.36}$$

with the new variables

$$\xi = aj \tag{II.37a}$$

$$\varphi = al \tag{II.37b}$$

$$\tau = D_0 a^2 t \tag{II.37c}$$

The first term in formula (II.36) is the kernel for the extended interval $-\infty < \xi, \varphi < +\infty$.

We deduce from the kernel (II.36) that

$$\Lambda_1(t) = \Lambda_1(0) + aD_0\Lambda_0 t(1 + 0(e^{-D_0 a^2 t})) \tag{II.38}$$

A comparison of equations (II.34) and (II.38) shows that the function $\Lambda_1(t)$, denoting the total amount of liquid condensed in the droplets as function of time, depends very sensitively upon the form of $\lambda(j)$. It is very hard to calculate analytically the kernel for a more realistic shape of λ than for that given by equations (II.29, 35). In the following section we evaluate the quantity Λ_1 directly from the differential equation (II.7).

II.4. The time evolution of the moments of the droplet distribution $f(j, t)$

Equations (II.27, 28) indicate that the time evolution (II.25) transforms a probability distribution into a probability distribution. We establish in this section a set of equations for the development in time of the mean value of the droplet size with respect to the droplet distribution (which we consider in this section to be normalized to one). We denote the mean value of the droplet size by

$$x(t) \equiv \langle j \rangle(t) \tag{II.39a}$$

higher moments by

$$\Delta_n(t) \equiv \langle (j - x(t))^n > (t) \quad n \in \mathbb{N}, n \geqslant 2 \tag{II.39b}$$

Using equation (II.7), we obtain the relation

$$\dot{x}(t) = \int_0^\infty dj f \frac{1}{\lambda} \frac{\partial}{\partial j}(D\lambda)$$

$$\left(\dot{x} \equiv \frac{dx}{dt}\right)$$

if we assume that the integrated parts

$$\left|_0^\infty jD\lambda \frac{\partial}{\partial j}\left(\frac{f}{\lambda}\right), \right|_0^\infty Df$$

can be neglected. A Taylor expansion of $\lambda^{-1}\, d/dj(D\lambda)$ yields the (formal) series

$$\dot{x}(t) = \psi(x) + \sum_{l=2}^{\infty} \frac{\Delta_l}{l!} \frac{d^l}{(dx)^l} \psi(x) \tag{II.40}$$

where the function ψ equals

$$\psi(j) = \frac{1}{\lambda(j)} \frac{d}{dj}(D(j)\lambda(j)) \tag{II.41}$$

Neglecting again the integrated parts, one obtains similarly

$$\frac{1}{n}\dot{\Delta}_n = \dot{x}\Delta_{n-1} + \sum_{l=0}^{\infty} (n-1) \frac{\Delta_{n+l-2}}{l!} \frac{d^l}{(dx)^l} D(x) + \sum_{l=0}^{\infty} \frac{\Delta_{n+l-1}}{l!} \frac{d^l}{(dx)^l} \psi(x) \tag{II.42}$$

for $n > 2$ ($\Delta_0 \equiv 1, \Delta_1 \equiv 0$).

If we now start with a distribution $f(j, 0)$ for which in equations (II.40, 42) the Δ_n with n bigger than some number N may be neglected, equation (II.40) and the equations (II.42) with $2 < n < N$ determine $x(t)$ and Δ_n with $2 < n < N$. The equation for Δ_{N+1} can serve to test the validity of the assumption that Δ_n with $n \leqslant N$ can still be neglected after a certain time.

If we start for instance with a δ-distribution all $\Delta_n = 0$ and we use

$$\dot{x} = \psi(x) \tag{II.43}$$

The equation

$$\dot{\Delta}_2 = 2D(x) + \left(\frac{d^2}{(dx)^2} D + 2\frac{d\psi}{dx}\right)\Delta_2 \tag{II.44}$$

together with the condition

$$\left| \frac{1}{2} \Delta_2(t) \frac{d^2\psi}{(dx)^2}(x(t)) \right| \ll \psi(x(t)) \tag{II.45}$$

may serve as test for the validity of (II.43).

We now discuss briefly equation (II.43). It is very reasonable to assume that for macroscopic droplets ($x > 10^{10}$)

$$\frac{d}{dx} \ln \lambda(x) = -\alpha$$

where α is given by (II.23b). (See f.i. [5]). Furthermore,

$$\frac{d}{dx} D(x) = 0\left(\frac{D}{x}\right) \ll |\alpha D|$$

D being a smooth function of x. We choose

$$\psi(x) = -\alpha D(x) \tag{II.46}$$

The function $D(x)$ is given by equations (II.10, 11, 12). With this choice of ψ equation (II.43) can be easily integrated and yield

$$q + \frac{1}{2} q^2 = -\alpha \frac{v_l \chi}{r_{cr}} (t - t_0) \tag{II.47}$$

with q defined by

$$q = \frac{r}{r_{cr}} \tag{II.48}$$

and χ, r_{cr} by equations (II.10, 11b). v_l is the volume of the liquid per molecule. The constant $v_l \chi r_{cr}^{-1} \cong 35\ s^{-1}$ for the example discussed at the end of Section II.2. We note that q is proportional to the condensation rate per unit area of the surface of the droplet.

Within the approximation (II.46) equation (II.44) can be written as

$$\frac{d}{dx} \Delta_2(x) = -\frac{2}{\alpha} - \frac{2}{\alpha} \frac{dD}{dx} \frac{\Delta_2}{D} \tag{II.49}$$

which yields ($x_0 = x(t)|_{t=0}$)

$$\Delta_2(x) = -\frac{2}{\alpha} D^{-2/\alpha}(x) \int_{x_0}^{x} dx'\, D^{2/\alpha}(x') \tag{II.50}$$

and

$$\Delta_2(x) = -\frac{2}{\alpha}(x - x_0) - \frac{1}{2}\left(\frac{2}{\alpha}\right)^2 (x - x_0)^2 \frac{d}{dx} \ln D + 0\left(\frac{D''}{D}(x - x_0)^3\right)$$

by a power series expansion of the integrand of (II.50). Observing that

$$\frac{D'}{D} = 0(x^{-1}) \qquad \frac{D''}{D} = 0(x^{-2})$$

we get for the inequality (II.45) that

$$\left|\frac{x - x_0}{\alpha x}\right| + \left|\frac{x - x_0}{\alpha x}\right|^2 < x \tag{II.51}$$

Equation (II.51) is fulfilled for the values of x and α ($x \gg 1$, $1 < \alpha < 2$) in which we are interested.

The reader may check that the equation (II.43) reproduces the formulas (II.34) and (II.38), if he inserts into (II.41) the forms of $\lambda(j)$ given by formula (II.29) and (II.35) and replaces $D(j)$ by the constant D_0.

The main advantage of the approach outlined in this section is that it conceptually leads back to a simple one-droplet-picture: it is enough to study the behaviour of a droplet which represents the mean water content per droplet. Its evolution is given essentially by equation (II.43). It is very satisfactory that the statistical effects disappear for macroscopic droplets as a consequence of equations (II.46) and (II.51).

The set of equations (II.40, 42) is suitable for numerical calculations.

III. The kinetics of homogeneous nucleation

III.1. The kinetic equation

'Homogeneous nucleation' means the process of the formation of droplets from a supersaturated vapor without condensation nuclei. We derive an expression for the kinetic equation using Frenkel's idea to consider droplets containing j molecules themselves as molecules of some substance A_j and fog as a composed system in which chemical reactions take place. These reactions are described by the equations

$$\sum_j a_j^r A_j = 0 \quad r \in \mathbb{N} \quad a_j^r \in \mathbb{Z} \tag{III.1}$$

The state of the r-th reaction is indicated by some reaction parameter Φ^r. The Φ^r are the independent particle number variables. The number f_j of particles in the substance A_j is given by

$$f_j = f_j^0 + \sum_r a_j^r \Phi^r \tag{III.2}$$

The differential of the inner energy U of the system is

$$dU = T\,dS - p\,dV + \sum_{jr} \mu_j a_j^r\, d\Phi^r$$

In equilibrium, the activities

$$\alpha^r = \sum_j \mu_j a_j^r$$

are zero.

If we keep the volume V and the inner energy U fixed, a change of the entropy is caused by the chemical reactions and equals

$$\frac{dS}{dt} = -\frac{1}{T}\sum_r \alpha^r \frac{d\Phi^r}{dt} \tag{III.3}$$

In accordance with the thermodynamics of irreversible processes, the 'currents' are, in a first approximation, linear combinations of the 'entropy conjugated potentials' $T^{-1}\alpha^r$ given by

$$\frac{d\Phi^r}{dt} = -\sum_s L^{rs}\frac{\alpha^s}{T} \tag{III.4}$$

in which the matrix of the coefficients is symmetric (Onsagers relations) [13].

Considering homogeneous nucleation, we have to account for at least two sets of chemical reactions:

(i) the growth of droplets by successive accumulation of single vapor molecules. These processes are described by the reaction equations

$$A_{j+1} - A_j - A_1 = 0, \quad j \geqslant 2 \tag{III.5a}$$

with reaction parameters

$$\Phi_1^{j+1} \tag{III.5b}$$

and activities

$$\alpha_1^{j+1} = \frac{\partial F}{\partial f_{j+1}} - \frac{\partial F}{\partial f_j} - \mu_A^{(0)} \tag{III.5c}$$

The Helmholtz free energy is given by equation (II.1), $\mu_A^{(0)}$ by (II.2) and

$$\left.\frac{\partial F}{\partial f_j}\right|_V = G_j + kT\ln f_j \tag{III.6}$$

ii) the direct formation of a droplet containing j molecules from the vapor:

$$A_j - jA_1 = 0, \quad j \geqslant 2 \tag{III.7a}$$

with reaction parameters

$$\Phi_2^j \tag{III.7b}$$

and activities

$$\alpha_2^j = \frac{\partial F}{\partial f_j} - j\,\mu_A^{(0)} \tag{III.7c}$$

We immediately get from the definition (III.2) ($d/dt \equiv \cdot$) that

$$\begin{aligned} \dot{f}_2 &= \dot{\Phi}_2^2 - \dot{\phi}_1^3 \\ \dot{f}_j &= \dot{\phi}_2^j + \dot{\phi}_1^j - \dot{\phi}_1^{j+1}, \quad j \geqslant 3 \end{aligned} \tag{III.8}$$

and

$$\dot{\Lambda}_0 \equiv \sum_{j=2}^{\infty} \dot{f}_j = \sum_{j=2}^{\infty} \dot{\Phi}_2^j \tag{III.9}$$

The equations (III.5) determine heterogeneous nucleation. The equations

$$\alpha_2^{j+1} = \alpha_2^{j+1} - \alpha_2^j = 0, \quad j \geqslant 2$$

determine the equilibrium distribution only up to a constant which is given by the total number Λ_0 of the nuclei. This is an external parameter of the system for hetero-

geneous nucleation. In the case of homogeneous nucleation at least one equation of the type (III.7) is present, forcing the α_2^j to be zero in equilibrium and yielding so the result obtained in Reference [5]:

$$f_j(\text{equilibrium}) \equiv \lambda_j = \exp \frac{1}{kT}(j\mu_A - G_j)$$

We now get the kinetic equation for homogeneous nucleation specifying statement (III.4) by postulating that the reaction rates Φ_1^j, Φ_2^j depend upon the activities α_1^j, α_2^j in the following manner

$$\dot{\Phi}_1^j = -\frac{d_j}{kT}\alpha_1^j \tag{III.10a}$$

$$\dot{\Phi}_2^j = -\frac{c_j}{kT}\alpha_2^j \tag{III.10b}$$

We assume that the matrix L^{rs} in equation (III.4) is diagonal, i.e. the chemical reactions are completely decoupled. We justify this postulat by showing that (III.10) agrees near equilibrium with the reaction equation obtained by kinetic considerations for dilute gases. This comparison will furnish the coefficients d_j, c_j (up to an ambiguity which is inherent in the method).

An elementary probability consideration leads to the following kinetic equation for the reaction (III.5a)

$$\dot{\Phi}_1^{j+1} = d_{j+1}^+ n_0 f_j - d_{j+1}^- f_{j+1} \tag{III.11}$$

where $n_0 = N_0/V$. The coefficients d_j^+ and d_j^- can in principle be calculated from the intermolecular potentials. A stationary solution of (III.11) is given by the conditions

$$d_{j+1}^+ n_0 f_j^s = d_{j+1}^- f_{j+1}^s$$

and equation (III.11) is near a stationary solution n_0^s, f_j^s

$$\dot{\Phi}_1^{j+1} = -d_{j+1}^- f_{j+1}^s \left(\frac{\delta f_{j+1}}{f_{j+1}^s} - \frac{\delta f_j}{f_j^s} - \frac{\delta n_0}{n_0^s} \right)$$

where

$$\delta n_0 \equiv n_0 - n_0^s, \quad \delta f_j \equiv f_j - f_j^s$$

But one has on the other hand for small deviations δn_0 and δf_j the relation

$$\frac{\delta f_{j+1}}{f_{j+1}^s} - \frac{\delta f_j}{f_j^s} - \frac{\delta n_0}{n_0^s} = \frac{\alpha_1^{j+1}}{kT}$$

because $\mu_A^{(0)} = kT \ln n_0$ up to a constant not depending on n_0 for a dilute gas if one neglects the dependence of G_j on n_0 in equation (III.6). We may, therefore, take

$$d_j = d_j^+ n_0 f_{j-1} \quad \text{or} \quad d_j = d_j^- f_j \tag{III.12}$$

in equation (III.10a). The two prescriptions are equivalent near equilibrium. We choose the second expression to get back equation (II.7).

The kinetic equation corresponding to the reaction (III.7a) is

$$\dot{\Phi}_2^j = c_j^+ V n_0^j - c_j^- f_j$$

which leads to the identifications

$$c_j = c_j^- f_j \quad \text{or} \quad c_j = c_j^+ V n_0^j$$

which are again equivalent near equilibrium. Since we are interested in studying the formation of droplets, we propose

$$c_j = V c_j^+ n_0^j \tag{III.13}$$

The equations (III.5, 6, 7, 8, 12, 13) finally lead to the kinetic equation for homogeneous nucleation ($c(j) = c_j^+$)

$$\frac{\partial}{\partial t} f(j, t) = \frac{\partial}{\partial j}\left\{ D(j)\lambda(j, t)\frac{\partial}{\partial j}\left(\frac{f(j, t)}{\lambda(j, t)}\right)\right\} + V c(j) n_0^j \left(1 - \frac{f(j, t)}{\lambda(j, t)}\right) \tag{III.14}$$

Being in the framework of a linearized theory, we have replaced in equation (III.14) $\ln x$ by $x - 1$. One avoids so an artificial singularity for $f = 0$.

The boundary conditions at $j = 0, j \to \infty$ are the same as for the equation (II.7) of heterogeneous nucleation: the production rate of droplets is given uniquely by the second term of equation (III.14).

Because only very small clusters are likely to be produced directly from the vapor, we replace

$$V c(j) n_0^j \quad \text{by} \quad C\delta(j - 0^+) \tag{III.15a}$$

where

$$\delta(j - 0^+) = \lim_{\epsilon \downarrow 0} \delta(j - \varepsilon) \tag{III.15b}$$

and

$$C = V \int_0^\infty dj\, c(j) n_0^j \tag{III.15c}$$

(See Section III.4 for a justification). C is the total current of direct droplet production from the vapor. But the effective production rate

$$\dot{\Lambda}_0(t) \equiv \int_0^\infty dj \frac{\partial}{\partial t} f(j, t) = C\left(1 - \frac{f(0, t)}{\lambda(0, t)}\right) \tag{III.16}$$

is smaller than C, because some of the droplets reevaporate.

Elementary kinetic and thermodynamic considerations yield the function $D(j)$ and the function $\lambda(j)$ up to a constant factor [5]. The constant C can be evaluated in a kinetic theory. (We do not calculate C in this paper.) The only quantity which is hardly accessible to theoretical calculations is $\lambda(0)$. We use $\lambda(0)$ as fit-parameter.

III.2. The nucleation rate

We assume in this section that the supersaturation of the system is held constant. With the help of propagator K of the equation (II.7), we express a special solution of the inhomogeneous equation

$$\frac{\partial f}{\partial t} - \frac{\partial}{\partial j}\left(D\lambda \frac{\partial}{\partial j}\left(\frac{f}{\lambda}\right)\right) = F(j, t)$$

in the form

$$\int_0^t ds \int_0^\infty dl\, K(j, l, t - s)F(l, s)$$

The solution of equations (III.14, 15) to the initial condition $f(j, 0) = 0$ obeys the equation

$$f(j, t) = \int_0^t ds\, K(j, 0^+, t - s)\dot{\Lambda}_0(s) \tag{III.17}$$

and the nucleation rate $\dot{\Lambda}_0$ is determined by the linear integral equation

$$u(t) = 1 - \int_0^t ds\, h(t - s)u(s) \tag{III.18a}$$

where

$$u = \frac{\dot{\Lambda}_0}{C} \tag{III.18b}$$

and

$$h(t) = \frac{C}{\lambda(0^+)} K(0^+, 0^+, t) \tag{III.18c}$$

The function $h(t)$ has the form $t^{-1/2}g(t)$, g being a smooth, bounded and non negative function, for the kernels in Section II.3B. One can show that in this case the integral equation (III.18a) has exactly one solution [14] which can be represented in a closed form by a Laplace transformation [15]:

$$u(t) = 1 - \int_0^t ds \frac{1}{2\pi i} \int_{m-i\infty}^{m+i\infty} dp \frac{e^{ps}}{1 + H(p)^{-1}} \tag{III.19a}$$

Equation (III.19a) is valid for any real m with

$$m > \inf_{m' \in \mathbb{R}} \left\{ \int_0^\infty e^{-mt} |h(t)|\, dt < \infty \right\} \tag{III.19b}$$

and $H(p)$ equals

$$H(p) = \int_0^\infty e^{-pt} h(t)\, dt \tag{III.19c}$$

We evaluate formula (III.19) for a simple model function

$$h(t) = b(\pi t)^{-1/2} e^{-a^2 t}, \quad a > 0 \tag{III.20}$$

which has a realistic shape for $t \to 0$ and $t \to \infty$ (a^2 may be identified with the smallest eigenvalue of the eigenvalue equation $Au = \omega u$. The operator A is defined in Appendix A. The proportionality to $t^{-1/2}$ comes from the normalization of the δ-distribution in formula (II.26b)). $H(p)$ is then

$$H(p) = b(p + a^2)^{-1/2}$$

With the substitutions $\sigma = sb^2, \tau = tb^2, \alpha = a/b, q = (p + a^2)/b^2, \tilde{m} = (m + a^2)/b^2,$

formula (III.19a) yields

$$u(\tau) = 1 - \frac{1}{1+\alpha} + \int_{\tau}^{\infty} d\sigma\, e^{-\alpha^2\sigma}\, \psi(\sigma)$$

We now remark that the function

$$\psi(x) = \frac{1}{2\pi i}\int_{\tilde{m}-i\infty}^{\tilde{m}+i\infty} dq\, \frac{e^{qx}}{q^{1/2}+1}$$

has the property that for positive values of the argument x

$$\lim_{x\to\infty} \psi(x) = 0$$

and that

$$-\frac{d\psi}{dx} + \psi = \frac{1}{2\pi i}\int_{\tilde{m}-i\infty}^{\tilde{m}+i\infty} dq\,(1-q^{1/2})\, e^{qx} = \frac{1}{x} - \frac{1}{\Gamma(-\frac{1}{2})}\cdot\frac{1}{x^{3/2}}$$

The solution is found to be

$$\psi(x) = \int_0^{\infty} dy\, e^{-y}\left(\frac{1}{x+y} + \frac{1}{2\sqrt{\pi}}\frac{1}{(x+y)^{3/2}}\right) \tag{III.21}$$

$$(\Gamma(-\tfrac{1}{2}) = -2\sqrt{\pi})$$

and

$$u(t) = \frac{a}{a+b} + \int_{b^2t}^{\infty} d\sigma \exp\left(-\frac{a^2}{b^2}\sigma\right)\psi(\sigma) \tag{III.22}$$

The function $u(t)$ falls monotonically from one to the stationary value $a/(a+b)$ after a time of the order of a^{-2} if $a/b \gg 1$, or of the order of b^{-2} if $a/b \ll 1$.

In the following section, we calculate directly the stationary nucleation rate.

III.3. The Becker-Döring nucleation rate

Equation (III.14) has the form of a continuity equation with a source term. Integration of (III.14) over the interval $0 \leqslant j \leqslant M$, and using $y'(0) = 0$ yields

$$\frac{d}{dt}\Lambda_{0M} + I_M = \int_0^M dj\, Vc(j) n_0^j \left(1 - \frac{f(j,t)}{\lambda(j)}\right) \tag{III.23a}$$

with

$$\Lambda_{0M} = \int_0^M dj\, f(j,t) \tag{III.23b}$$

and

$$y(j,t) = \frac{f(j,t)}{\lambda(j)} \tag{III.23c}$$

$$I_M = -D\lambda \frac{\partial y}{\partial j}\bigg|_M \tag{III.23d}$$

Two remarks are crucial for the following:

(i) The direct formation of droplets from the vapor occurs only for very small droplets (with $j < j_1$ say). $\dot{\Lambda}_{0M} + I_M$ becomes independent from M for $M > j_1$.

(ii) In the case of supersaturation $(D\lambda)^{-1}$ has a sharp maximum at $j_0 > j_1$ (see Section (III.4); j_0 lies between 40 and 90) and goes to zero very rapidly if j deviates from j_0.

We now assume that f can be approximated by a stationary solution of (III.14) in some interval $0 < j < M$, for $M > j_0$. (A justification of this assumption is given in Appendix C). $\dot{\Lambda}_{0M}$ is then zero and the total droplet production rate $\dot{\Lambda}_0$ equals I_M. The general solution of the equation

$$\frac{d}{dj}\left(D\lambda \frac{dy}{dj}\right) = - Vc(j)n_0^j(1 - y) \equiv F(j) \tag{III.24a}$$

with the boundary conditions

$$y'(0) = 0 \quad \text{and} \quad y(M) = y_M \tag{III.24b}$$

can be found using the Greensfunction $u(j, l)$ which is determined by the equations

$$\frac{\partial}{\partial j}\left(D\lambda \frac{\partial u}{\partial j}\right) = \delta(j - l)$$

$$\left.\frac{\partial u}{\partial j}\right|_{j=0} = 0, \quad u(M, l) = u_M, \quad \forall l \geqslant 0$$

The solution $u(j, l)$ equals

$$u(j, l) = \begin{cases} u_M + \displaystyle\int_M^j \frac{dj'}{D\lambda} & j \geqslant l \\ u_M + \displaystyle\int_M^l \frac{dj'}{D\lambda} & j \leqslant l \end{cases}$$

We write the general solution of equations (III.24) in the form

$$y = \int_0^M dl\, u(j, l)F(l) = \left(u_M + \int_M^j \frac{dj'}{D\lambda}\right)\int_0^M dl F(l) + \int_j^M \frac{dj'}{D\lambda}\int_{j'}^M dl\, F(l)$$

Since

$$\int_0^M dl\, F(l) = -I_M$$

for a stationary process and, according to the remarks (i) and (ii),

$$\left|\int_j^M \frac{dj'}{D\lambda}\int_{j'}^M dl\, F(l)\right| \ll \left|\int_j^M \frac{dj'}{D\lambda}\int_0^M dl\, F(l)\right|$$

the stationary solution is given by

$$y(j) = y_M + I_M \int_j^M \frac{dj'}{D\lambda}$$

We insert now this stationary solution into equation (II.23a) and get

$$I_M = \int_0^M dj\, Vc(j)n_0^j \left(1 - \left(y_M + I_M \int_j^M \frac{dj'}{D\lambda}\right)\right)$$

which determines I_M. We can first extend the range of integration of j' from zero to M, because $(D\lambda)^{-1}(j) \cong 0$ if $Vc(j)n_0^j$ is different from zero.

If moreover $M \gg j_0$ then $y_M = (f/\lambda)(M) \cong 0$ and the ranges of integration of j and j' can be extended from 0 to ∞. This yields the following equation for the nucleation rate I

$$I = \left(\int_0^\infty \frac{dj}{D\lambda} + \left(\int_0^\infty dj\, Vc(j)n_0^j\right)^{-1}\right)^{-1} \tag{III.25}$$

Equation (III.25) reduces to

$$I = I_0 \equiv \left(\int_0^\infty \frac{dj}{D\lambda}\right)^{-1} \tag{III.26}$$

in the case that

$$\frac{C}{I_0} = \int_0^\infty \frac{dj}{\lambda D} \cdot \int_0^\infty dj\, Vc(j)n_0^j \gg 1 \tag{III.27}$$

i.e. if the 'production current' C of droplets from the vapor is sufficiently high (see equations (III.13, 15c)). Equation (III.26) is generally accepted to be true, mainly because the fact escaped attention that two things determine the stationary nucleation rate I: the production current C and the manner how the reactions (III.5a) transport the droplet flow I (which is indicated by the quantity (III.26)).

Equation (III.26) was first derived by Becker and Döring [3] using the kinetic equations (III.11) but imposing somehow artificial and in fact unnecessary restrictions on the stationary process they considered. Equation (III.26) was also derived by Frenkel [9] starting from a stationary solution of equation (II.7) and from rather mysterious boundary conditions at $j = 0$. Frenkel's derivation is shorter than Becker's but not a progress from our point of view.

III.4. Nucleation rate for a simple droplet model

In ref. [5], we derived the expression

$$\lambda(j) = \frac{V}{V^*} \exp\left(-\alpha j - \gamma j^{2/3}\right) \tag{III.28}$$

α and γ are as in (III.21, 22), V^* is an unknown parameter with the dimension of a volume.

Only droplets whose size lies far beyond the critical radius r_{cr} given by formula (II.11) are important for the calculation. Following equation (II.10), we set D equal to

$$D = 3wp^S(2\pi mkT)^{-1/2}\left(\frac{4\pi}{3}\right)^{1/3} v_l^{2/3} j^{2/3} \equiv E \cdot j^{2/3} \tag{III.29}$$

($E = 2.4 \times 10^6$ sec^{-1} for the values of the constants involved given at the end of Section II.2)
Introducing $z = j^{1/3}$ as a new variable, we get

$$\int_0^\infty \frac{dj}{D\lambda} = \frac{3V^*}{EV} \int_0^\infty dz \exp(\alpha z^3 + \gamma z^2)$$

We expand the exponential around its maximum ($\alpha < 0$!)

$$Z_0 = j_0^{1/3} = -\frac{2}{3}\frac{\gamma}{\alpha} \tag{III.30}$$

and evaluate the integral of equation (III.26) by the saddelpoint method. This yields

$$\frac{I_0}{V} = \sqrt{\frac{\pi}{\gamma}\frac{E}{3V^*}} \exp\left(-\frac{4}{27}\frac{\gamma^3}{\alpha^2}\right) \tag{III.31}$$

[9]. This formula represents well the qualitative behaviour of nucleation. $(4/27)\gamma^3 \cong 76$ and the nucleation rate should depend strongly on the supersaturation α. Beyond critical supersaturation practically no nucleation occurs, above this value nucleation becomes very violent. This behaviour is indeed observed in experiments.

The nucleation rate I_0/V has been measured. The magnitude of the parameter V^* may, therefore, be estimated by the equation (III.31)

Table 1

T [°K]	I_0/V [cm^{-3}]	S	$-\alpha$	p^S [mb]	σ [dyn cm^{-1}]	γ	j_0	V^* [10^{-x} cm^3] x	
261	$\sim 10^2$	5.03	1.67	2.44	77.6	9.93	64	19.8	Volmer & Flood
263	10^5	5.0	1.61	2.86	77.3	9.82	68	23.4	Frey
261	10^2	4.36	1.47	2.44	77.6	9.93	92	25.9	Sander & Damköhler
261	10^6	6.60	1.89	2.44	77.6	9.93	43	18.6	Barnard
261	10^3	5.70	1.74	2.44	77.6	9.93	55	18.6	Madonna & al.
238	10^3	6.40	1.86	0.313	81.4†)	11.4	69	26.6	Madonna & al.

†) Extrapolated value.

The supersaturation parameter S is defined as

$$S \equiv e^{-\alpha}$$

Values of the nucleation rate I_0/V versus the supersaturation parameter S are taken from Mason's book [16] the other constants from the Landolt-Börnstein tables [10], [11], [12]. Mason judges the measurements of Barnard and of Madonna to be the most reliable. The small value of V^* at 238°K may be caused by a too high extrapolated value of the surface tension ($x = 18.6$ would correspond to $\sigma = 72$ dyn cm^{-2}) following Mason, but we see no reason why V^* could not depend

quite strongly on the temperature. Another reason may be that for $T = 238°$ the saturation density n_0 of the vapor is so small that $C \lesssim I_0$. One must then use the full formula (III.25) and take into account that $I(\alpha)$ saturates for high values of $|\alpha|$. We, therefore, choose $V^* \cong 2.5 \times 10^{-13}$ cm^3.

III.5. Fluctuations and nucleation

The quantity

$$\Delta G_{cr} = kT \frac{4}{27} \frac{\gamma^3}{\alpha^2}$$

is the amount of Gibbs free energy ΔG_{cr} required to form a droplet of Kelvin's critical size from the vapor. *One* droplet of critical size is metastable in a supersaturated vapor, a smaller droplet evaporates, and a bigger one grows. Equation (III.31) is often written [7], [17] in the form

$$\frac{I_0}{V} = \text{const. exp} - \frac{\Delta G_{cr}}{kT} \tag{III.32}$$

One considers exp $(-1/kT\,\Delta G_{cr})$ as Boltzmann's factor proportional to the frequency of 'fluctuations of overcritical size' which are believed alone to generate droplets which can grow. In contrast 'undercritical fluctuations' should decay (see [3], [9]).

I think this is a misleading statement. Phase transitions, or more general, chemical reactions are not caused by fluctuations. Nobody would consider the chain $0, 0_2, 0_3, \ldots$ to be caused by density fluctuations. The notion 'fluctuation' has a precise meaning in statistical physics. It indicates how well the mean values are defined which are the constituent quantities of thermodynamics. They impose an under limit to the size of systems which can reasonably be described by thermodynamics. It is a crucial point in our derivation of the formula (III.25) for the stationary nucleation rate that only the very smallest clusters are formed directly from the vapor and that all others are formed by successive accumulation. All clusters grow in the average if the system is supersaturated, the 'undercriticals' grow too.

Consider the difference of the chemical potentials (II.5)

$$\frac{\mu_A^{(0)} - \mu_A^{(j)}}{kT} = -\frac{\partial}{\partial j} \ln \frac{f}{\lambda} \tag{III.33}$$

which governs the rate of condensation on a droplet. Inserting the stationary droplet distribution

$$f = I\lambda \int_j^\infty \frac{dj'}{D\lambda} \tag{III.34}$$

of Section III.3 into formula (III.33) yields

$$\frac{\mu_A^{(0)} - \mu_A^{(j)}}{kT} = \left(D(j)\lambda(j) \int_j^\infty \frac{dj'}{D\lambda} \right)^{-1} \tag{III.35}$$

The function $(D\lambda)^{-1}$ has a sharp maximum near Kelvin's critical size j_0. The 'driving force' (III.33) equals, therefore,

$$\frac{\mu_A^{(0)} - \mu_A^{(j)}}{kT} = \begin{cases} \dfrac{I_0}{(D\lambda)(j)} \quad (\simeq 0) & \text{for } j < j_0 \\ \dfrac{I_0}{2(D\lambda)(j_0)} \quad \left(= \dfrac{9}{8}\alpha^2\gamma^{-5/2}\right) & \text{for } j = j_0 \\ \dfrac{d}{dj}\ln D\lambda \quad \left(= -\alpha - \frac{2}{3}\gamma j^{-1/3} + \frac{2}{3}j^{-1}\right) & \text{for } j > j_0 \end{cases} \tag{III.36}$$

The values in the brackets correspond to the expressions (III.28), (III.29), (III.31) for λ, D and I_0. The approximation for $j > j_0$ is obtained by replacing the function $(D\lambda)(j')$ by

$$(D\lambda)(j)\cdot\exp\left(\frac{d\ln D\lambda}{dj}(j' - j)\right) \tag{III.37}$$

One may check that for $j' > j > j_0$ and with the expressions (III.28), (III.29) for the functions λ and D

$$(D\lambda)(j') > (D\lambda)(j)\cdot\exp\left(\frac{d\ln D\lambda}{\mu j}(j' - j)\right) \tag{III.38}$$

if one chooses the appropriate values for the involved constants ($\gamma = 8$, $j_0 > 40$). The inequality (III.38) implies that $\mu_A^{(0)} - \mu_A^{(j)}$ increases monotonically with j.

The condensation rate $\dot{n}_j$ on a droplet of size j (II.5) is a positive and monotonically increasing function of j, although very small for $j < j_0$. For $j > j_0$, we obtain the first order approximation (II.43) of Section II.4.

The growth of the droplets is a dynamical process: more molecules condense on a droplet than evaporate from it. The quantity $\dot{n}_j$ stands for the mean condensation rate on a droplet of size j. This mean value is the quantity of interest, not the story of an individual droplet which may evaporate even when $\dot{n}_j > 0$.

The basic quantity is the stationary nucleation rate I_0

$$I_0 = \left(\int_0^\infty \frac{dj}{D\lambda}\right)^{-1} \simeq \min_j D\lambda \tag{III.39}$$

due to the functional forms of λ and D. The Gibbs' droplet model yields the expression (III.28) for the function $\lambda(j)$ [5], and allows to go from equation (III.39) to (III.32).

I do not think that the transition from equation (III.39) to (III.32) conceals deep physical insights. It may well be that $\lambda(j)$ increases monotonically in j for systems other than liquid droplets in gas. One would then write I_0 more appropriately in the form

$$I_0^{-1} = \sum_{j=2}^{\infty} (D_j\lambda_j)^{-1} \simeq \sum_{j=2}^{n} (D_j\lambda_j)^{-1}$$

where n is a small number, than in the form (III.32) and nobody would introduce the notions of metastability and of over- or under-critical fluctuations.

IV. Conclusion

It is not the fact that one droplet can be at best metastable in contact with a supersaturated vapor that is the guiding physical insight in nucleation theory, but

that an ensemble of droplets can be thermodynamically stable. This allows the development of the thermodynamics of fog. Starting from the equilibrium theory, one derives the basic nucleation equations by directly applying the principles of the thermodynamics of irreversible processes.

The crucial physical concept in the derivation of the formula (II.1) for the Helmholtz free energy of fog is the notion of identical particles. We call particles identical if they share the same physical properties, i.e. if the result of an experiment does not depend upon which particles were used. This definition of 'identical' makes sense in classical as well as in quantum physics. It leads in the classical framework to the statistical postulate of Reference [5] which shows that – and in what respects – droplets of the same size j can be treated as identical particles. Fog and clouds represent the consequences of the notion 'identical particles' on a macroscopic scale – a phenomenon similar to the zero point pressure of a Fermi gas.

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Appendix A

We reformulate the initial value problem (II.14, 15) in the language of vectors in a Hilbert space and their time evolution due to a differential equation of the type

$$\frac{dy}{dt} = Ay$$

The linear operator A

$$A: u \to -\frac{1}{\lambda}\frac{\partial}{\partial j}\left(D\lambda \frac{\partial u}{\partial j}\right)$$

is symmetric in the Hilbert space $L_2(\lambda\, dj, \mathbb{R}^+)$ of complex functions $u(j)$ for which

$$\int dj\, |u(j)|^2 \lambda(j) < \infty \quad \text{and} \quad \left.\frac{du}{dj}\right|_{j=0} = 0$$

with respect to the scalar product

$$(u, v) = \int_0^\infty dj\, \lambda(j) u^*(j) v(j)$$

A is furthermore a non-negative operator (the functions $D(j)$ and $\lambda(j)$ are positive for $0 < j < 0$).

$$(u, Au) = \int_0^\infty dj\, D(j)\lambda(j) \left|\frac{du}{dj}\right|^2 \geqslant 0$$

and can be enlarged to a non-negative selfadjoint operator (Theorem of Friedrichs [18]). We may expand every initial condition $y(j, 0) \in L_2(\lambda\, dj, \mathbb{R}^+)$ in terms of (generalized) eigenfunctions of A and obtain a Fourier analysis of the problem.

The condition $(u, Au) = 0$ implies $u = \text{const.}$ If the system is saturated or undersaturated λ decreases exponentially for large j (see Reference [5], Sections III.2 and III.3) and the integral

$$\int_0^\infty dj\, \lambda(j) < \infty$$

$u = \text{const.}$ is an eigenfunction of A with eigenvalue zero and y achieves a constant equilibrium value different from zero. In the case of supersaturation λ increases exponentially and the above integral diverges. The operator A is then strictly positive and $y(j, t)$ goes to zero almost everywhere as t goes to infinity.

To be more explicit: we are interested in initial conditions $y(j, 0) > 0$. This implies $y(j, t) > 0\ \forall t > 0$ (See appendix B). Let us denote by $L_p^+(\mathbb{R}^+, \lambda\, dj)$ the space of all functions u: $\mathbb{R}^+ \to \mathbb{R}^+$ for which

$$\|u\|_p = \left(\int_0^\infty dj\, \lambda(j) u^p(j) \right)^{1/p} < \infty$$

Consider now $y(j, t) \in L_p^+(\mathbb{R}^+, \lambda\, dj)$ for which

$$\lim_{j \to \infty} D\lambda y^{p-1} \frac{\partial y}{dj} = 0\ \forall t$$

for some p in a neighborhood of 1. One easily calculates

$$(\| y(t) \|_p)^{p-1} \frac{d}{dt} \| y(t) \|_p = (1 - p) \int_0^\infty dj\, D\lambda y^{p-2} \left(\frac{dy}{dj} \right)^2$$

which yields

$$\frac{d}{dt} \| y(t) \|_p \equiv 0 \quad \text{if } p = 1$$

$$\frac{d}{dt} \| y(t) \|_p \left\{ \begin{matrix} > 0 & \text{if } p < 1 \\ < 0 & \text{if } p > 1 \end{matrix} \right\} \quad \text{or} \quad y(j, t) \text{ is constant in } j$$

This illustrates the tendency of the distribution y to spread out and to flatten under the time evolution.

Appendix B

We consider the differential equation

$$\frac{\partial}{\partial t} y(j, t) - \frac{1}{\lambda(j)} \frac{\partial}{\partial j} \left(D(j)\lambda(j) \frac{\partial}{\partial j} y(j, t) \right) = 0 \tag{B.1}$$

in the region $0 < t < \infty$, $0 < j < \infty$ and with the boundary conditions

$$\begin{aligned} &\lim_{j \to 0} D(j)\lambda(j) \frac{\partial}{\partial j} y(j, t) = 0, \quad t > 0 \\ &\lim_{j \to \infty} y(j, t) = 0, \quad t > 0 \end{aligned} \tag{B.2}$$

The functions $D(j)$ and $\lambda(j)$ can be expanded in infinite power series

$$0 < D(j) = j^{\delta} \sum_{k=0}^{\infty} \frac{D_k}{k!} j^k \quad \delta \in \mathbb{Z}, \delta < 2$$

and

$$\ln \lambda(j) = \sum_{k=0}^{\infty} \frac{L_k}{k!} j^k$$

which converge for j in some interval $0 < j < I$, $I > 0$.

Proposition: The kernel $K(j, l, t)$ of the propagator of the differential equation (B.1) with the boundary conditions (B.2) is non-negative:

$K(j, l, t) \geqslant 0$ for $j, l, t \geqslant 0$

Proof: (a) We first prove the following

Theorem: [19] Let G denote the rectangle $0 \leqslant j \leqslant J$, $0 \leqslant t \leqslant T$

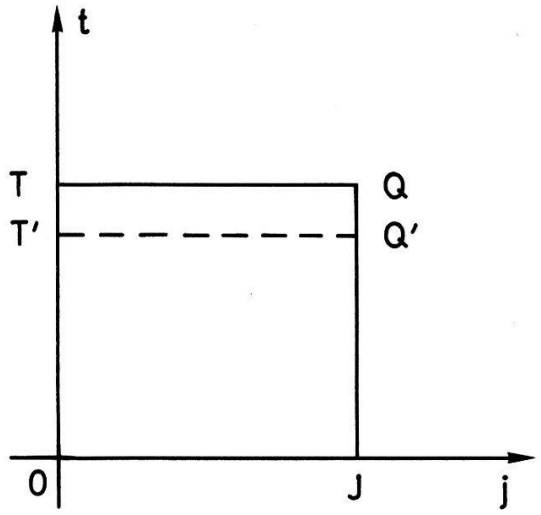

Figure 1.

and $u(j, t)$ a solution of the differential equation

$$Bu \equiv \frac{\partial u}{\partial t} - D(j) \frac{\partial^2 u}{(\partial j)^2} - C(j) \frac{\partial u}{\partial j} = 0,$$

$D(j) > 0$ for $0 \leqslant j \leqslant J$

in G (u is at least twice continuously differentiable in j and once in t for j, t in G).

The function $u(j, t)$ attains its maximum or minimum in G on the line $L = \overline{\text{TOJQ}}$.

Proof of the theorem: Let us assume that the absolute maximum M of u lies in the interior of G or on the line $\overline{\text{TQ}}$. Let m be the maximum of u on L. We now consider the function

$$v(j, t) = u(j, t) + k(T - t)$$

where

$$0 < k < \frac{M - m}{T} \tag{B.3}$$

The absolute maximum of v is bigger or equal to M and the maximum of v on L is smaller than M by construction. The absolute maximum of v still lies in the interior of G or on the line $\overline{TQ}$.

(i) The absolute maximum of v lies at some point j', t' in the interior of G. This implies

$$\left.\frac{dv}{\partial t}\right|_{j',t'} = 0, \qquad \left.\frac{dv}{dj}\right|_{j',t'} = 0, \qquad \left.\frac{\partial^2 v}{(\partial j)^2}\right|_{j',t'} \leqslant 0$$

which yields

$$0 \leqslant Bv = Bu - k = -k$$

in contradiction to assumption (B.3).

(ii) The absolute maximum of v lies at the point j', T on $\overline{TQ}$. Then

$$\left.\frac{dv}{dt}\right|_{j',T} \geqslant 0, \qquad \left.\frac{dv}{\partial j}\right|_{j',T} = 0, \qquad \left.\frac{\partial^2 v}{(\partial j)^2}\right|_{j',T} \leqslant 0$$

and $0 \leqslant Bv$ as before.

The absolute maximum of the function u (and equally of the function $-u$) in the rectangle G lies, therefore, on the line L. QED.

(b) We now study a solution of the differential equation (B.1) which fulfills the boundary condition

$$\lim_{j \to 0} D(j)\lambda(j) \frac{\partial}{\partial j} u(j, t) = 0, \quad \text{for} \quad 0 \leqslant t \leqslant T \tag{B.4}$$

in the neighborhood of $J = 0$. We write u as a power series in j

$$u(j, t) = v(t) + j^{\kappa} \sum_{k=0}^{\infty} \frac{w_k(t)}{k!} j^k, \quad \kappa \neq 0$$

where the coefficients $v(t)$ and $w_k(t)$ are at least once continuously differentiable with respect to t, and insert u into the differential equation (B.1). This yields

$$\frac{dv}{dt} - w_0 D_0 \kappa(\kappa + \delta - 1) j^{\kappa+\delta-2} + 0(j^{\kappa+\delta-1}) = 0$$

as a consequence of the chosen value of δ. The boundary condition (B.4) implies that

$$\kappa + \delta - 1 > 0$$

Therefore, we obtain

$$\kappa = 2 - \delta > 0$$

and

$$u(j, t) = v(t) + \frac{1}{D_0(2 - \delta)} \frac{d}{dt} v(t) j^{2-\delta} + 0(j^{3-\delta}) \tag{B.5}$$

(c) We finally consider the boundary conditions

$$\lim_{j \to 0} D\lambda \frac{\partial u}{\partial j} = 0 \quad \text{for} \quad 0 \leqslant t \leqslant T$$

$$u(j, 0) \geqslant 0 \quad \text{for} \quad 0 \leqslant j \leqslant J, \qquad u(J, t) \geqslant 0 \quad \text{for} \quad 0 \leqslant t \leqslant T$$

Then $u(0, t) \geqslant 0$ for $0 \leqslant t \leqslant T$.

Proof: Let us assume that there is a point t with $0 < t \leqslant T$ for which $u(0, t) < 0$. Then points t_0, t_1 exist with the following properties

$$0 \leqslant t_0 < T$$

$$u(0, t) \geqslant 0 \quad \text{for all } t \text{ with } \quad 0 \leqslant t \leqslant t_0$$

$$u(0, t) \geqslant 0 \quad \text{for all } t \text{ with } \quad 0 \leqslant t \leqslant t_0' \quad \text{implies} \quad t_0' \leqslant t_0$$

and

$$t_1 = T \quad \text{if} \quad \frac{du(0, t)}{dt} \neq 0 \quad \text{for} \quad t_0 < t \leqslant T$$

or

$$t_0 < t_1 \leqslant T \quad \text{and} \quad \left.\frac{du(0, t)}{dt}\right|_{t_1} = 0$$

$$t_0 < t_1' < T \quad \text{and} \quad \left.\frac{du(0, t)}{dt}\right|_{t_1'} = 0 \quad \text{imply } t_1' > t_1$$

By construction, $u(0, t)$ decreases monotonically from $u(0, t_0) = 0$ to $u(0, t_1) < 0$. We choose now a point T' in $t_0 < T' < t_1$. $u(0, T')$ is the minimum of u on the line $L' = \overline{\mathrm{T'OJQ'}}$ and

$$\left.\frac{du(0, t)}{dt}\right|_{T'} < 0$$

As a consequence of equation (B.5)

$$u(j, T') = u(0, T') + \frac{1}{D_0(2 - \delta)} \frac{d}{dt} u(0, t)|_{t=T'} j^{2-\delta} + 0(j^{3-\delta}) < u(0, T')$$

for a sufficiently small but positive value of j. This contradicts the theorem. Therefore, $u(0, t) \geqslant 0$ for $0 \leqslant t \leqslant T$. QED.

From the theorem one concludes that the boundary conditions (c) imply that $u(j, t) \geqslant 0$ for every point j, t in the rectangle G. This implies the statement which we wanted to prove – namely that the kernel is not negative for the rectangle G. But the finiteness of J was not assumed in this proof; it is valid also for the infinite interval $0 \leqslant j < \infty$. QED.

It is a consequence of the result obtained in c) that the only solution of the differential equation (B.1) is $y(j, t) = 0$ for the boundary conditions (B.2) and the initial condition $y(j, 0) = 0$ for $0 \leqslant j$. Thus the initial value problem (B.1, 2) and $y(j, 0) = f(j)$ has only one solution.

For the functions λ and D given by equations (III.28) and (II.11), we write the differential equation (B.1) and the boundary condition (B.2) in the variable $z = j^{1/3}$. One may verify that the proof stays valid.

Appendix C

We write equation (III.14) in the form

$$\frac{\partial y}{\partial t} - \frac{1}{\lambda}\frac{\partial}{\partial j}\left(D\lambda\frac{\partial y}{\partial j}\right) = \delta(j - 0^+)\frac{\dot{\Lambda}_0(t)}{\lambda(0)}$$

where 0^+ is an arbitrarily small but positive number.

If we now substitute

$$y = w + \dot{\Lambda}_0(t)\int_j^\infty \theta(j' - 0^+)\frac{dj'}{D(j')\lambda(j')}$$

we get the equation

$$\frac{\partial w}{\partial t} - \frac{1}{\lambda}\frac{\partial}{\partial j}\left(D\lambda\frac{\partial w}{\partial j}\right) = -\ddot{\Lambda}_0(t)\int_j^\infty \theta(j' - 0^+)\frac{dj'}{D(j')\lambda(j')} \tag{C.1a}$$

with boundary conditions

$$w(\infty, t) = y(\infty, t) = 0, \quad \left.\frac{\partial w}{\partial j}\right|_{j=0} = \left.\frac{\partial y}{\partial j}\right|_{j=0} - \left.\frac{\dot{\Lambda}_0\theta(j - 0^+)}{D(j)\lambda(j)}\right|_{j=0} = 0 \tag{C.1b}$$

If the system achieves a stationary nucleation rate ($\ddot{\Lambda}_0 = 0$) the equations (C.1) are completely equivalent to the equations discussed in Section II.3 and in Appendix A; we conclude that $w \to 0$ as $t \to \infty$. If the supersaturated system therefore achieves a stationary nucleation rate, this stationary value is given by formula (III.25).

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