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# Size distribution of new-phase particles during transient condensation of a supercooled gas

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The homogeneous nucleation of the liquid phase upon rapid cooling of a gas is considered in the framework of the Zel'dovich-Frenkel theory, and the time-dependent distribution function of nuclei in size space and the nucleation rate are determined. It is shown that in the transient case a certain modification must be made to the basic kinetic equation at high supersaturations of the gas to allow for the discrete number of molecules in a nucleus. The form of the distribution function is found in the leading and next-higher approximations in the reciprocal of the activation barrier. Comparison with a numerical simulation shows that the results are quite accurate.

## INTRODUCTION

According to Zel'dovich,<sup>1</sup> the formation of new-phase nuclei can be described by a kinetic equation of the Fokker-Planck type in "size space"

$$\frac{\partial f}{\partial t} = -\frac{\partial j}{\partial g}, \quad j = -D(g)N(g)\frac{\partial f}{\partial g} \frac{f}{N}. \quad (1)$$

Here  $g$  is the number of molecules in a nucleus (the "size"),  $f(g, t)$  is the nonequilibrium distribution function,  $j(g, t)$  is the flux in size space,  $D$  is the diffusion coefficient, and  $N$  is the equilibrium distribution function, which is related to the change in the free energy of the system upon formation of a nucleus of a given size:  $N \sim \exp[-\Phi/kT]$ . The critical size  $g_*$  corresponds to the maximum of the function  $\Phi(g)/kT$ . In the theory considered here, this maximum value (which is assumed large) determines the activation barrier of the nucleation process.

At fixed parameters  $g_*$ ,  $\Phi_*$ , etc., the system has a steady equilibrium distribution

$$f(g) = \frac{1}{2} N(g) \operatorname{erfc}\left(\frac{g-g_*}{\Delta}\right) \quad (2)$$

with a size-independent value of the flux

$$j_{ss} \equiv J = \frac{D(g_*)N(g_*)}{\Delta\sqrt{\pi}}, \quad \Delta = \left(-\frac{1}{2kT} \frac{\partial^2 \Phi}{\partial g^2} \Big|_{g_*}\right)^{-1/2}. \quad (3)$$

( $\Delta$  is the width of the critical region).

In reality, changes in the external conditions and depletion of the initial phase by the nuclei that form cause the level of metastability of the system and hence the nu-

cleation process to become time dependent. Transience in the formation of the largest nuclei can be particularly important, since these nuclei will govern the breakoff of nucleation and the transition of the system to the asymptotic regime.<sup>3,4</sup> The transient problem has hitherto been considered mainly from the standpoint of relaxation to the steady distribution (see review<sup>5</sup>).

In the present study, new-phase nucleation is investigated in the case of a time-dependent level of metastability of the initial phase; the characteristic times for changes in the activation barrier here can be comparable to the time for relaxation to the steady distribution, and so transient effects can be important. Situations of this type can occur in molecular beams, which are characterized by high rates of cooling,<sup>6</sup> in condensed media,<sup>7</sup> and at temperatures near a critical point,<sup>8</sup> where the relaxation to the steady distribution slows down.

As in the steady-state treatment,<sup>1</sup> the quantity  $\epsilon = \Delta/g_*$  is taken as the small parameter of the problem. The condition  $\epsilon \ll 1$  is satisfied if the height  $\Phi_*/kT$  of the activation barrier is so large that its square root  $(\Phi_*/kT)^{1/2}$  is also large.

In Sec. 1 we construct asymptotically (in  $\epsilon$ ) exact expressions for the distribution function and the flux of nuclei in size space. We determine the transient nucleation rate.

In Sec. 2 we consider the nucleation of a liquid phase at high supersaturations of the gas, when the initial equation applies only in a comparatively small neighborhood of the critical size. We obtain a kinetic equation which is valid for all sizes below the critical size and goes over to Eq. (1) in the critical region, and we construct the time-dependent solution to the leading and next-higher orders in  $\epsilon$ . The results are compared with a numerical simulation.

In the Appendix we give an asymptotically exact solution for the relaxation to steady nucleation.

### 1. TRANSIENT DISTRIBUTION OF NUCLEI IN SIZE SPACE AND THE RATE OF NUCLEATION

In the classical theory of nucleation<sup>3</sup> the nuclei are treated macroscopically, and the energy  $\Phi$  can be divided into surface and volume parts

$$-\frac{\Phi(g)}{kT} = g \ln S - lg^{2/3}, \quad l = (4\pi)^{1/3} (3v_L)^{2/3} \frac{\sigma}{kT}. \quad (4)$$

Here  $S$  is the degree of supersaturation of the gas,  $v_L$  is the molecular volume of the liquid phase, and  $\sigma$  is the coefficient of surface tension. The basic small parameter of the problem,  $\varepsilon = \Delta/g_*$ , is of the form  $(\Phi_*/3kT)^{-1/2}$ . At moderate gas densities the diffusion coefficient  $D(g)$  in Eq. (1) is given as  $\alpha_c \beta s_g$ , where  $\alpha_c$  is the condensation coefficient and  $\beta s_g$  is the frequency of collisions between gas molecules and the nuclear surface  $s_g$ .

If the thermodynamic parameters of the gas (temperature, pressure, etc.) are time dependent, the coefficients in the expression for the work of formation of a nucleus in (4) will vary with time. In the leading approximation in  $q/kT$  ( $q$  is the heat of the phase transition per molecule)<sup>11</sup> it is necessary to consider the time derivatives only of quantities containing  $\ln S$ , with the result

$$\frac{\partial}{\partial t} \frac{\Phi(g)}{kT} = \frac{g}{g_*} \frac{\partial}{\partial t} \frac{\Phi_*}{kT}. \quad (5)$$

We shall show that the function (5), which contains a time derivative of the asymptotically large parameter  $\varepsilon^{-2}$ , plays the governing role in the description of the transient nucleation. As a quantitative measure of the level of transience one can take the quantity

$$n = -\tau_{\text{rel}} \frac{\partial}{\partial t} \frac{\Phi_*}{kT},$$

where the time  $\tau_{\text{rel}} = \Delta^2/2D_*$  characterizes the relaxation to the steady distribution (see Appendix).

Before we start on the solution of the problem, let us formulate the basic assumptions.

We assume that the characteristic times for changes in the thermodynamic parameters of the initial phase that do not exhibit anomalies on crossing the line of phase equilibrium are much larger than  $\tau_{\text{rel}}$ . However, the characteristic time for changes in the height of the activation barrier is not assumed to be long compared to  $\tau_{\text{rel}}$ , and we accordingly keep the quantity  $n$  in the expressions given below.

We transform the initial equation (1) to the new unknown function  $v = f/N$  and "size"  $u = g/g_*$

$$\frac{1}{2} \varepsilon^2 \frac{\partial}{\partial u} \frac{D}{D_*} \frac{\partial v}{\partial u} + \frac{D}{D_*} \frac{\partial v}{\partial u} \frac{\Phi'}{\Phi_*} - nuv = \tau_{\text{rel}} \frac{\partial v}{\partial t} + \frac{\varepsilon^2}{2} nu \frac{\partial v}{\partial u}, \quad \Phi' \equiv \frac{\partial \Phi}{\partial u}. \quad (6)$$

The boundary conditions on Eq. (6) are determined from the conditions that the kinetic and equilibrium distribution functions agree for nuclei of extremely small

sizes<sup>1</sup> and that the total number of nuclei in the system be finite:

$$v(0, t) = 1, \quad v(u, t) \rightarrow 0, \quad u \rightarrow \infty. \quad (7)$$

Because the coefficients of Eq. (6) vary little over a time  $\tau_{\text{rel}}$  and the boundary conditions (7) are independent of time, for nuclei which are not too much larger than the critical size a quasisteady size distribution is established which is described by the equation

$$\varepsilon^2 \frac{\partial}{\partial u} \frac{D}{D_*} \frac{\partial v}{\partial u} + \frac{D}{D_*} \frac{2\Phi'}{\Phi_*} \frac{\partial v}{\partial u} - 2nuv = \varepsilon^2 nu \frac{\partial v}{\partial u}. \quad (8)$$

The difference from the corresponding steady-state equation is characterized by the parameter  $n$ .

We solve Eq. (8) by the method of "matched asymptotic expansions" (Ref. 10).

Outside the critical region,  $\Phi^1$  is not small, and the terms proportional to  $\varepsilon^2$  in Eq. (8) can be neglected. In this case

$$\ln v = n \int_0^u du \frac{D_* \Phi_*'}{D \Phi_*}. \quad (9)$$

For  $u \rightarrow 1$ , Eq. (9) has the asymptotic form

$$\ln v = n \ln(1-u) + nC, \quad (10)$$

$$C = \int_0^1 du \left\{ u \frac{D_* \Phi_*'}{D \Phi_*} - \frac{1}{u-1} \right\} = \frac{25}{12} - \ln 3. \quad (11)$$

Near  $u = 1$ , where the "outer" solution (9) is not valid, we transform to the "inner"  $\bar{z} = (u-1)/\varepsilon$ . To leading order in  $\varepsilon$ , Eq. (8) reduces to the equation

$$\frac{\partial^2 v}{\partial \bar{z}^2} + 2\bar{z} \frac{\partial v}{\partial \bar{z}} - 2nv = 0, \quad (12)$$

which was considered in Ref. 11. The decaying solution of (12) for  $\bar{z} \rightarrow \infty$  is of the form

$$v(\bar{z}) = \frac{1}{2} A_n i^n \text{erfc}(z), \quad (13)$$

where  $i^n \text{erfc}(z)$  is the multiple probability integral.<sup>12</sup>

The coefficient  $A_n$  in the last expression is determined from the condition that the asymptotic value of the inner solution (13) for  $\bar{z} \rightarrow \infty$  agree with that of the outer solution (10) for  $u \rightarrow 1$ :

$$A_n = \Gamma(n+1) \varepsilon^n e^{nC}. \quad (14)$$

Finally, we write out the expression for the distribution function in terms of the original variables:

$$f(g, t) = \frac{1}{2} N(g, t) \Gamma(n+1) \left( \frac{\Phi}{3kT} \right)^{-n/2} e^{nC} i^n \text{erfc} \left( \frac{g-g_*}{\Delta} \right). \quad (15)$$

This equation agrees with (2) in the steady-state limit  $n \rightarrow 0$ .

If the cooling rate of the gas is characterized by the quantity  $\omega = -\partial \ln T / \partial t$ , then it is easy to show that

$$n = \frac{1}{\lambda} \frac{\omega}{\alpha_g} \varepsilon^{2/3}, \quad (16)$$

where  $\lambda = \sigma v_L^{2/3} / q$  (for simple liquids  $\lambda \sim 1/6$ , and for water far from the critical temperature  $\lambda \sim 1/10$ );  $\nu \sim \beta v_L^{2/3}$  is the frequency of intermolecular collisions. It follows from (16) that the condition  $n \gg 1$  can be satisfied even at cooling rates which are small compared to the intermolecular collision frequency:  $\omega \sim \lambda \alpha_0 g_*^{-5/3} \nu \ll \nu$ .

Solution (15) applies for  $z \ll \varepsilon^{-1}$ , or  $(g - g_*) / g_* \ll 1$ . An estimate of the derivative  $\partial v / \partial t$  in the region of maximum sizes yields a condition for admissible values of  $n$ :

$$n \ll 2(\Phi_*/kT) / \ln(\Phi_*/kT). \quad (17)$$

A comparison of (17) with the condition of substantial transience  $n \gg 1$  implies that solution (15) has meaning in an asymptotically wide interval of cooling rates.

We have been considering the initial stage of nucleation, when the height of the activation barrier decreases with time ( $n > 0$ ). Analogous estimates for the final stage stage ( $n < 0$ ) show that the solution applies only for  $n > -1$ ; for smaller  $n$  no quasisteady regime is established (see Appendix). However, in the stage  $n \ll -1$  an exponentially small amount of the liquid phase is formed; consequently, the intense nucleation can be described entirely by solution (15).

Let us consider the flux of nuclei in size space. Near  $g_*$  we have to leading order in  $\varepsilon$

$$j(g, t) = -\frac{D_* N_*}{\Delta} e^{z^2} \frac{\partial v}{\partial z} = J \frac{\sqrt{\pi}}{2} A_* e^{z^2} i^{n-1} \operatorname{erfc}(z), \quad (18)$$

where  $J$  is the size-independent steady-state value of the flux (3). The function  $e^{z^2} i^{n-1} \operatorname{erfc}(z)$  for  $z \rightarrow +\infty$  has the asymptotic form  $(2/\sqrt{\pi})(2z)^{-n}$ , whence it follows for  $1 \ll z \ll \varepsilon^{-1}$  that

$$j = J A_* (2z)^{-n} \quad (19)$$

[the upper bound on  $z$  derives from the applicability conditions for Eq. (12)].

The expressions obtained for the distribution function and flux cannot be used for "large" nuclei with  $g - g_* \gg g_*$ . Here, however, the macroscopic character of the behavior of the large nuclei is a simplifying circumstance, so that one does not have to consider equations of type (1) containing a second derivative with respect to the "coordinate" (size). To find the size distribution of the nuclei in this case it is sufficient to know their rate of formation  $I$  and initial size  $g_0$ .

Let us (formally for now) define the rate of nucleation  $I$  as the flux at  $g = g_0$ . The size distribution of the large nuclei is of the form

$$f(g, t) = g^{-1} j(g_0, t - \tau(g, g_0)),$$

where  $\tau(g, g_0)$  is the time over which a nucleus grows to size  $g$ . The ambiguity associated with the choice of  $g_0$  vanishes if the latter satisfies the conditions  $g_0 - g_* \gg \Delta$ . In this case the drift component of the flux is substantially larger than the diffusion component and is given by asymptotic expression (19), which should thus be regarded as the transient nucleation rate  $I$ . In the original variables

$$I = J \Gamma(n+1) e^{n\varepsilon} \left(\frac{\Delta}{2g_*}\right)^n \left(\frac{g_0 - g_*}{\Delta}\right)^{-n}. \quad (20)$$

Unlike the steady nucleation rate  $J$ , Eq. (20) depends on the initial size  $g_0$ , which can be chosen arbitrarily in the interval  $\Delta \ll g_0 - g_* \ll g_*$ ; as we have said, this ambiguity does not affect the "observable" quantities. We note that in a purely steady-state treatment<sup>1</sup> the question of the choice of initial size can be answered only to logarithmic accuracy; here this quantity is uniquely related to the nucleation rate.

It is shown in the Appendix [see (A.9)] that upon establishment of a steady distribution the flux remains practically zero during an "incubation" time

$$t_i = \tau_{\text{rel}} \left\{ \ln \frac{2z}{\varepsilon} - C' \right\}$$

According to our assumptions

$$J \exp(-nt_i / \tau_{\text{rel}}) = J(t - t_i)$$

and we can write Eq. (20) in the form

$$I = J(t - t_i(g_0)) \exp(n(C - C')) \Gamma(n+1). \quad (21)$$

Thus the rate of formation of nuclei of size  $g_0$  is determined mainly by the steady-state nucleation rate at the time  $t - t_i(g_0)$ . The insignificant (from an asymptotic standpoint) corrections  $\exp[n(C - C')]$  and  $\Gamma(n+1)$  arise because of the renormalization of the incubation and relaxation times for a system with a time-dependent level of metastability. Within the domain of application of the expressions we have obtained, nucleation rate (21) naturally is smaller than the steady-state value  $J(t)$ . The difference vanishes for  $n \ll 2 / \ln(\Phi_*/kT)$ .

Formula (21) also applies to the description of nucleation in other physical situations in which the expressions for the work of formation of a nucleus, the diffusion coefficient, etc. can be different from the ones considered. The relaxation time here is given as before by the expression  $\tau_{\text{rel}} = \Delta^2 / 2D_*$ , and the constant  $C'$  which appears in the incubation time  $t_i$  is evaluated from the macroscopic equations for the decomposition of a nucleus, viz., formula (A.6). Certain differences arise only in the calculation of  $C$  if the expression for  $\partial(\Phi/kT)/\partial t$  is more complicated than (5). We note, however, that relation (5) is typical, since it is the coefficient multiplying the volume term that primarily determines the level of metastability of the system.

## 2. LARGE SUPERSATURATIONS OF THE GAS. REFINEMENT OF THE SOLUTION WITH ALLOWANCE FOR THE DISCRETE NUMBER OF MOLECULES IN A NUCLEUS

The domain of application of the initial equation (1) is restricted to a neighborhood of width  $\Delta$  near the critical size<sup>13</sup>; it is easily verified, for example, that outside this neighborhood the quantity  $D \partial \ln N / \partial g$  does not correspond to the macroscopic growth rate  $\dot{g}$  when the supersaturation is large,  $\ln S \gg 1$ . In the steady-state case the domain of application of equation (1) can be extended to all subcritical sizes, since the solution is determined by the behavior of the coefficients in (1) specifically near  $g_*$ . In the steady case, as is clear from the previous discussion, the values of the coefficients for all  $g < g_*$  contribute

to the solution, and Eq. (1) must be modified so that it also holds for small nuclei with  $g < g_* - \Delta$ .

The change in the kinetic distribution function with allowance for only the dominant processes of condensation and evaporation of a single molecule can be described by the following system of kinetic equations<sup>1</sup>:

$$\frac{df}{dt} = j_g - j_{g+1}, \quad j_g = D_{g-1} N_{g-1} \left( \frac{f_{g-1}}{N_{g-1}} - \frac{f_g}{N_g} \right). \quad (22)$$

Equation (1) follows immediately from (22) upon replacement of the first differences by first derivatives. Such a replacement, however, is not possible everywhere, since outside the critical region the equilibrium distribution function  $N(g)$  [and, for  $g < g_* - \Delta$ , the function  $f(g)$  itself] changes by a quantity of the order of unity when  $g$  is replaced by  $g \pm 1$ . This circumstance can be taken into account rather simply for the function  $N(g)$ : the finite difference terms should be kept as they are and not replaced by derivatives in the expressions which contain only the known functions. To obtain a correct continuum equation for the kinetic distribution function it is necessary to transform from the function  $f$  to a new unknown function which varies smoothly in size space. In the subcritical region  $g < g_*$ , as we see from the solution obtained earlier,  $v(g, t) = f/N$  is a smoothly-varying function for which Eq. (22) implies the equation

$$\frac{\partial v}{\partial t} + v \frac{\partial \ln N}{\partial g} = \frac{\partial}{\partial g} D \frac{\partial v}{\partial g} + D \Psi \frac{\partial v}{\partial g} - \frac{1}{2} D \Psi \frac{\partial^2 v}{\partial g^2}, \quad (23)$$

where  $\Psi = 1 - N_{g-1}/N_g$  [the last term in (23) is retained in order to get the corrections of order  $\epsilon$ ]. Equation (23) holds not only in the critical region, where it is practically the same as Eq. (1), but also in the region of small sizes, where Eq. (1) does not apply.

The growth of large nuclei with sizes  $g \gg g_* + \Delta$ , for which this equation does not apply, can be described by macroscopic equations with  $g = D\Psi^2$ .

The rest of the calculation is conveniently done in the variables  $x = (g/g_*)^{1/3}$ . Equation (23) becomes

$$\frac{1}{2} \left( \frac{\epsilon}{3} \right)^2 \frac{\partial^2 v}{\partial x^2} \left( 1 - \frac{1}{2} \Psi \right) + \frac{\Psi}{\ln S} x^2 \frac{\partial v}{\partial x} - n v x^3 = \tau_{el} x^2 \frac{\partial v}{\partial t} + \frac{\epsilon^2}{6} x^3 \frac{\partial v}{\partial x} n. \quad (24)$$

In analogy with the previous discussion we find that outside the critical region

$$\ln v = n \int_0^x dx x^3 \frac{\ln S}{\Psi}. \quad (25)$$

To leading order in  $\epsilon$ , the equation for the function  $v(z)$  retains the form (12) near  $g_*$ , and the solution is of the form (13), (14), where

$$C = \int_0^1 dx \left( \frac{\ln S}{\Psi} x^3 - \frac{3x^2}{x^3 - 1} \right) \approx \frac{25}{12} - \ln 3 + \frac{\ln S}{8} - \frac{(\ln S)^2}{144}. \quad (26)$$

We note that this solution differs substantially from that obtained in Sec. 1 only at extremely large supersaturations or at a high level of transience ( $n \ln S \sim 8$ ).

In taking into account the discrete number of molecules one should, generally speaking, allow for the higher terms in the asymptotic expansion of the solution in  $\epsilon$ . In the outer solution (25), the corrections that arise are of order  $\epsilon^2$  and do not have to be taken into account, since this quantity is extremely small for macroscopic nuclei. On the other hand, the corrections to the solution in the critical region are of order  $\epsilon$  and must be taken into account for an accurate description of the behavior of the distribution function near  $g_*$  (see the comparison with the numerical simulation below).

Near  $g_*$  we seek a solution of the form

$$v(z) = v_0(z) \exp \left\{ \frac{\epsilon}{3} \frac{v_1(z)}{v_0(z)} \right\}, \quad z = \frac{3(x-1)}{\epsilon}, \quad (27)$$

where  $v_0(z)$  is the solution of (13) with a renormalized value [corresponding to (26)] of the constant  $C$ .

Substituting (27) into quasisteady equation (24) and keeping terms through order  $\epsilon$ , we obtain a linear inhomogeneous equation for  $v_1(z)$ , from which

$$\begin{aligned} \frac{2v_1(z)}{A_n} &= -4n(n+1) i^{n+1} \operatorname{erfc}(z) \left( 1 + \frac{\ln S}{8} \right) \\ &- \frac{1}{2} i^{n-1} \operatorname{erfc}(z) \left( 1 + \frac{n-1}{2} \ln S \right) - \frac{1}{12} i^{n-3} \operatorname{erfc}(z). \end{aligned} \quad (28)$$

For  $z \rightarrow -\infty$  the inner solution of (27), (28) has the asymptotic behavior

$$v(z) \sim \epsilon^n |z|^n \exp \left\{ nC - \frac{4}{3} n |z| \epsilon \left( 1 + \frac{\ln S}{8} \right) \right\},$$

which to the leading and next-higher orders in  $\epsilon$  corresponds to the asymptotic behavior of solution (25) for  $x \rightarrow 1$ .

The accuracy of the above solution was illustrated by numerically solving system of equations (22) in an expanding gas volume. Here the degree of transience of the process was characterized by a variable  $n$ . Curve 1 in Fig. 1 was obtained for  $n \approx 1$  ( $n = 1.025$ ); for the example considered, this value corresponded to the following values of the parameter:  $g_* \approx 55$ ,  $\ln S \approx 1.06$ ,  $\epsilon \approx 0.32$ . Curves 2 and 3 show the leading (13) and the next-higher approximation in  $\epsilon$  without allowance for the discreteness. Curve 4 shows the solution (27), (28), which takes into account the discrete number of molecules in a nucleus; we see that this solution practically coincides with the "exact" solution inside the critical region.

## CONCLUSIONS

### 1. Transient nucleation of a new phase, like steady

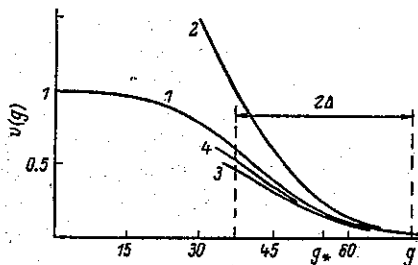


FIG. 1

nucleation, can be described to asymptotic accuracy in the height of the activation barrier.

2. For a time-dependent level of metastability of the initial phase, the transience of the nucleation process is basically characterized by the quantity  $n$ , which specifies the change in the height of the activation barrier over a time  $\tau_{rel}$  ( $\tau_{rel}$  is the time for relaxation to steady nucleation). Substantial transience ( $n \gg 1$ ) can occur even for gas cooling rates which are extremely small compared to the frequency of intermolecular collisions.

For sizes smaller than the critical size or not too much larger, a quasisteady distribution is established which is determined by the instantaneous configuration of the potential relief and its first time derivative. In the limit  $n \rightarrow 0$  the expressions obtained for the distribution function and flux correspond to the familiar steady-state solution of Zel'dovich, Eqs. (2), (3).

3. Under transient conditions the nucleation rate differs from the steady-state rate by a pre-exponential factor which depends on the choice of the initial size of the incipient nuclei. However, this ambiguity does not affect the "observable" characteristics of the process (the distribution function of the large nuclei). By establishing the relationship between the initial size of a nucleus and the nucleation rate, one can go beyond the traditional "logarithmic accuracy" inherent to the purely time-independent treatment, in which the initial size of the nucleus is strictly undetermined.

4. The discreteness of the number of molecules in a nucleus primarily affects the macroscopic growth rate of the nucleus. This is reflected in the distribution of nuclei in the critical region only in the transient case at high supersaturations of the gas. In the general case allowance for the discreteness should be accompanied by another asymptotic expansion in the reciprocal of the activation barrier. Here the next-higher (after the leading) approximation usually gives sufficient accuracy for practical purposes.

## APPENDIX

### RELAXATION TO THE STEADY DISTRIBUTION

Let us rewrite the initial equation (1) for a time-independent equilibrium distribution  $N(g)$  in the variables  $u = g/g_*$  and  $v = f/N$ :

$$\epsilon^2 \frac{\partial}{\partial u} D \frac{\partial v}{\partial u} + D \frac{2\Phi'}{\Phi_*^2} \frac{\partial v}{\partial u} = \Delta^2 \frac{\partial v}{\partial t}. \quad (\text{A.1})$$

After a Laplace transformation

$$V(u, p) = \int_0^\infty dt e^{-pt} v(u, t)$$

Eq. (A.1) reduces to the equation

$$\epsilon^2 \frac{d}{du} D \frac{dV}{du} + D \frac{2\Phi'}{\Phi_*^2} \frac{dV}{du} = \Delta^2 V p \quad (\text{A.2})$$

with the boundary condition  $V(0, p) = p^{-1}$ , which follows from (7). Solving (A.2) in analogy with (8) by the method of matched asymptotic expansions, we find the outer solutions<sup>3)</sup> ( $1 - u \gg \epsilon$ )

$$V(u, p) = p^{-1} \exp\{-p\tau(u)\}, \quad (\text{A.3})$$

$$\tau(u) = -\int_0^u du/\dot{u}, \quad \dot{u} = -\frac{D}{kT} \frac{\partial \Phi}{\partial g} g_*^{-1},$$

where  $\tau(u)$  is the decomposition time of a nucleus, and the inner solution [ $z = (u - 1)/\epsilon$ ,  $|z| \ll \epsilon^{-1}$ ].

$$V(z, p) = \frac{1}{2} B(p) i^m \operatorname{erfc}(z), \quad m = p \frac{\Delta^2}{2D_*}. \quad (\text{A.4})$$

From the matching condition for asymptotes (A.4) at  $z \rightarrow -\infty$  and (A.3) for  $u \rightarrow 1$ , we find

$$B(p) = p^{-1} \Gamma(m+1) e^{m\phi'} \epsilon^m, \quad (\text{A.5})$$

$$C' = \int_0^1 du \left\{ \frac{2D_*}{\Delta^2} \frac{1}{u} - \frac{1}{u-1} \right\},$$

which gives

$$V(z, p) = \frac{1}{2} \frac{\Delta^2}{2D_*} \epsilon^m e^{m\phi'} \Gamma(m) i^m \operatorname{erfc}(z). \quad (\text{A.6})$$

Function (A.6) has a pole at  $m = 0$ , corresponding to steady-state solution (1). The nearest pole  $m = -1$  ( $p = -2D_*/\Delta^2$ ) determines the maximum relaxation time

$$\tau_{rel} = \Delta^2 / 2D_*. \quad (\text{A.7})$$

Let us determine how the steady distribution is established in the above-critical region  $z \gg 1$ . Here (A.6) can be replaced by the asymptotic expression

$$V(z, p) \approx \frac{1}{\sqrt{\pi}} \frac{\Delta^2}{2D_*} \epsilon^m e^{m\phi'} \Gamma(m) e^{-z^2} (2z)^{-m-1}. \quad (\text{A.8})$$

The poles of the function (A.8) are located at the points  $m = 0, -1, -2, \dots$  and have residues (with respect to  $m$ ) of  $(-1)^{-m}/(-m)!$ . Introducing the "incubation time"

$$t_i = \tau_{rel} (\ln(2z/\epsilon) - C') \quad (\text{A.9})$$

we have for  $t \gg t_i - \tau_{rel} \ln z^2$

$$v(z, t) \approx \frac{1}{\sqrt{\pi}} \frac{\epsilon^{-z^2}}{2z} \sum_{(-m)!} \exp\left\{m \frac{t - t_i(z)}{\tau_{rel}}\right\}. \quad (\text{A.10})$$

Formally the sum in (A.10) is defined only for  $-m \ll z^2$  [otherwise asymptotic expression (A.8) is invalid], but because of the rapid convergence in (A.10) one can extend the summation to  $-\infty$  to get

$$v(z, t) \approx \frac{1}{\sqrt{\pi}} \frac{\epsilon^{-z^2}}{2z} \exp\left\{-\exp\left(-\frac{t - t_i}{\tau_{rel}}\right)\right\}.$$

In an analogous way, we get for the flux

$$j(z, t) = J \exp \left\{ -\exp \left( -\frac{t - t_i(z)}{\tau_{rel}} \right) \right\}. \quad (\text{A.11})$$

Over a time  $t < t_i$  the flux is practically zero.

Under transient conditions a function  $2\nu D^* u$  is added to (A.1) [see (6)].

In analogy with the previous case we get

$$V_n(z, p) = \frac{1}{2m} \tau_{rel}^{m+n} e^{m\sigma + n\sigma} \Gamma(m+n+1) i^{m+n} \operatorname{erfc}(z). \quad (\text{A.12})$$

where the constant  $C$  is found in Sec. 1. The pole at  $m = 0$  leads to quasisteady regime (15), which sets in over a time which is determined by the pole at  $m = -n - 1$ :

$$\tau_{rel}(n) = \tau_{rel}/(n+1). \quad (\text{A.13})$$

In the initial stage of nucleation ( $n > 0$ ) the relaxation time is shorter than the time for relaxation to the steady distribution, while in the final stage of nucleation ( $n < 0$ ) it is longer, and for  $n \leq -1$  the quasisteady regime discussed in this paper does not arise at all.

<sup>1</sup>Unlike  $\epsilon$ , the parameter  $q/kT$  does not play a fundamental role but only streamlines the calculations somewhat.

<sup>2</sup>A kinetic equation which holds for  $g > g^* - \Delta$  and goes over to (1) in the critical region was obtained in Ref. 14; the discreteness of the variable  $g$  was taken into account in Refs. 13 and 15 in a study of the relaxation to the steady distribution.

<sup>3</sup>Applying the inverse Laplace transformation to (A.3) gives the obvious result  $v(u, t) = \Theta(t - \tau(u))$ , where  $\Theta$  the theta (step) function.

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## Shaping of electron beams from convex thermionic cathodes

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The shaping of electron beams is studied for guns having highly curved convex cathodes. It is shown that the curvature of the cathode causes a specific aberration which increases the beam cross section. The current density distribution in the plane of the smallest cross section of the beam (the crossover) is found, and it is shown that the current density at the center of the crossover, and with it the average brightness of the beam, falls off with increasing curvature of the cathode.

The theory of low-current electron guns is well developed for flat thermionic cathodes. It has been shown that the current density distribution in the plane of the smallest beam cross section is Gaussian and that the size of the spot is independent of the area of the emitting surface on the cathode.

Many electron guns utilize convex or sharp-tip thermionic cathodes having a large curvature of the emitting part of the cathode surface. There are various reasons for this. Highly curved cathodes permit the electric field near the cathode to be shaped in such a way that it limits the region on the cathode from which the emitted electrons enter the beam. This limits the total currents in the supply and stabilization circuits.

For highly curved cathodes one can obtain strong

electric fields which (through the Schottky effect) increase the emission current density and hence the brightness of the electron beam. Here there are important technical questions in connection with the fabrication of various special cathodes. Experiments show that the spot dimensions in such guns depend substantially on the curvature of the cathode and the surface area from which emission occurs.

The shaping of electron beams in convex cathodes having a significant curvature of the emitting surface differs substantially from the shaping of electron beams from a flat cathode surface on account of the spherical aberration due to the cathode curvature. This effect has been studied in the model of imaginary point sources mainly for field-emission cathodes.<sup>1,2</sup> In Ref. 1 there is