

# Steady-state and transient nucleation of a new phase in a first-order transition

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Usp. Fiz. Nauk **155**, 329–355 (June 1988)

Examples of crystallization of glasses and of the condensation of excitons to form an electron-hole liquid in germanium are used to study the kinetics of nucleation of a new phase. There are considerable advantages in tackling such model systems rather than other systems undergoing a first-order phase transition. Attention is drawn to two different nucleation regimes: transient and quasisteady-state. Special consideration is given to nucleation in an open system from which nuclei of the new phase may be removed rapidly as a result of diffusion or drift to absorbing walls. In such cases very strong supersaturation may be reached and the threshold of the appearance of a new phase may be independent of temperature.

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What do we know about the fox?  
Nothing!  
(And even then not everything...)  
B. Zakhoder

## INTRODUCTION

First-order phase transitions are well-known, but the nucleation processes, i.e., the processes of appearance of the minimum volumes of a new phase capable of subsequent growth (known as critical nuclei) have not been investigated thoroughly. This is because the amount of matter participating in nucleation is very small and frequently a nucleus consists of several molecules or atoms; the nucleation time is usually much shorter than the characteristic phase separation time. Finally, in many cases the nucleation process is heterogeneous, i.e., it is associated with impurities and defects in a homogeneous ("parent") medium.

Among the very large number of papers on the kinetics of first-order phase transitions (some idea of the number of these papers can be gained from reviews and monographs<sup>1-5</sup>), we shall consider only those which address the specific question of the relationship between steady-state and transient nucleation; on the experimental side, we shall consider crystallization of glasses and condensation of excitons in semiconductors. The macroscopic behavior of these systems is related directly to the nucleation kinetics and these systems approach most closely the conditions assumed in the simplest (linear) formulation of the problem of nucleation when the concentration of the new phase is low and has practically no influence on the initial state of the parent medium.

We shall consider the specific case of a gas-liquid transition. If the transition occurs in an impure gas, where the role

of nucleation centers may be played by—for example—dust specks, the process of appearance of a new phase exhibits no singularities: when the gas density exceeds the saturated vapor density, a drop of a liquid forms at a dust speck and this drop grows subsequently and then the entire increase in the number of particles in the system occurs in this drop. However, if a gas is pure, the process of nucleation is accompanied by supersaturation, as first pointed out by Gibbs<sup>6</sup> and related to the fact that a small drop has (because of the curvature of its surface) a binding energy per particle lower than in a drop of macroscopic size. If the supersaturation is weak, a critical nucleus is large and consists of a large number of particles. All the drops of size less than critical evaporate faster than the rate of their growth. Therefore, a drop larger than critical can appear only as a result of a macroscopic (and therefore very unlikely) fluctuation.<sup>1)</sup>

The kinetics of a transition is governed by the nucleation rate, i.e., by the number of critical nuclei of the new phase which appear in a unit volume per unit time. In the case of the topics under discussion the phenomenon of supersaturation is responsible for the leading exponential factor in the expression for the nucleation probability. This factor is governed solely by thermodynamic quantities: the free energy of the phases and the surface tension.

Calculation of the absolute nucleation rate may require determination also of the preexponential factor; like the delay time, this preexponential factor is governed by transport effects. Depending on the situation, these effects may be dif-

fusion, heat conduction, viscosity, etc. Moreover, there may be corrections due to vibrational, rotational, and translational motion of a nucleus. This is the reason for the complexity of the problem.

Two time intervals describe the transition kinetics. One of them is the average time between the appearances of nuclei in the parent medium; this interval is inversely proportional to the volume of the homogeneous phase. The other time interval is independent of the volume and is equal to the delay time from the moment of supersaturation to the attainment of the average (called steady-state) nucleation rate. Although this time interval is usually short, it is of fundamental importance and one of our aims will be to discuss the experimental situations in which it is possible to separate steady-state and transient nucleation (Sec. 2).

The second problem which we shall discuss is related to steady-state nucleation in an open system (Sec. 3). It has recently become clear that the concept of the process of nucleation as the appearance of a larger than critical (supercritical) nucleus as a result of fluctuations (because of competition between evaporation and attachment of atoms) is of limited usefulness. In particular, if a transition occurs in an open system from which liquid drops can be removed (for example, by diffusion or drift in an external field) and the time spent by a drop in the bulk of the system is short compared with the characteristic nucleus formation time, the supersaturation may be very high and unrelated to evaporation and attachment. Under these conditions we can speak of a kinetic branch of a phase transition which is practically independent of temperature and which corresponds to a very high (for example, thousandfold) supersaturation.

In the concluding section we shall consider briefly some of the still unsolved problems.

## 1. KINETIC CONCEPT OF NUCLEATION

In many cases of practical importance the smallest viable (i.e., capable of subsequent spontaneous growth) drop (bubble or crystallite) consists of a large number of particles and the properties of such a drop may be described macroscopically; we can deal with the transition simply by finding the probability of appearance of viable nuclei in a unit volume per unit time.

An elementary definition of the required probability is well known. The probability  $W$  of a fluctuation which alters by  $\Delta\Phi$  the free energy (or the thermodynamic potential) of the system is given by the expression<sup>8</sup>

$$W \propto \exp \left( - \frac{\Delta\Phi}{kT} \right).$$

If a fluctuation is deemed to be the appearance in a gas of a liquid drop<sup>1</sup> consisting of  $\nu$  particles, we have

$$\Delta\Phi = -\nu kT \ln \frac{n}{n_s} + 4\pi\sigma r^2, \quad (1)$$

where  $\sigma$  is the surface tension of the liquid;  $r = (3\nu/4\pi n_0)^{1/3}$  is the radius of a drop;  $n_0$  is the drop density.

The first term in Eq. (1) is equal to the product of the number of particles in a drop and the difference between the chemical potentials of the gas and liquid; these potentials can be described, considering the condensing vapor as an ideal gas, in terms of the gas density  $n$  and the saturated vapor concentration  $n_s$ .

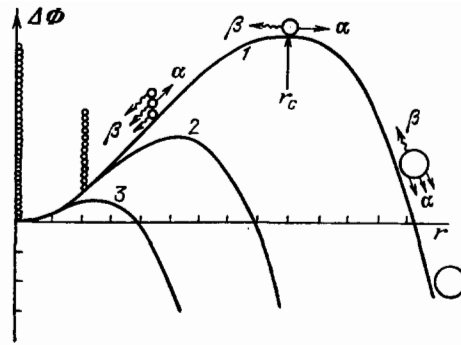


FIG. 1. Dependence on the drop radius  $r$  of the difference  $\Delta\Phi$  between the thermodynamic potentials of a homogeneous gaseous phase and of a heterophase system. Here,  $r_c$  is the radius of a critical nucleus; the degree of saturation obeys  $(n/n_s)_1 < (n/n_s)_2 < (n/n_s)_3$ ;  $\alpha$  and  $\beta$  are the rates of attachment and evaporation of atoms, respectively.

The second term in Eq. (1) allows macroscopically for the fact that in a drop of finite size the binding energy of particles in the surface layer is less than the binding energy of the particles located deeper in the drop. Therefore, this term is always positive.

If the vapor is supersaturated ( $n > n_s$ ), the first term in Eq. (1) is negative and proportional to the volume of the drop, whereas the second term is positive and proportional to the surface, where  $\Delta\Phi(r)$  represents a barrier which has to be overcome by the condensing system (Fig. 1). The barrier height is  $\Delta\Phi_{\max} = (4\pi/3)\sigma r_c^2$ , where  $r_c$  is the radius of a critical nucleus corresponding to the maximum of the thermodynamic potential. Equating the derivative  $d\Delta\Phi/dr$  to zero, we find that

$$r_c = \frac{2\sigma}{n_0 kT \ln(n/n_s)}. \quad (1')$$

Consequently, the density of a gas in equilibrium (which is unstable!) with a drop of radius  $r$  is<sup>2)</sup>:

$$n = n_s \exp \frac{2\sigma}{n_0 r kT}.$$

The nucleation rate, i.e., the number of nuclei that overcome a barrier per unit volume per unit time, is proportional to the "equilibrium" density of such nuclei, i.e., it is proportional to  $W$ :

$$j = c \exp \left( - \frac{\Delta\Phi_{\max}}{kT} \right). \quad (2)$$

Equation (2) for the nucleation rate was proposed by Volmer and Weber.<sup>9</sup> The preexponential factor  $c$  encountered in this approach is undefined; however, there is no need to determine it accurately because the exponential function depends very strongly on the degree of supersaturation and temperature.

Better understanding of nucleation as a kinetic process arose from the work of Kaishev and Stranskiĭ,<sup>10</sup> Becker and Döring,<sup>11</sup> and Zel'dovich.<sup>12</sup> In the kinetic approach an analysis is made of the motion of a drop in the space of drop sizes  $r$  in a "potential" field  $\Delta\Phi(r)$ . The general nature of such motion becomes clear from a mechanical analogy: a drop located on the left-hand side of  $\Delta\Phi(r)$ , where  $r < r_c$  (Fig. 1), rolls down to the left, i.e., it evaporates and is converted back to the gas, whereas a drop of radius  $r > r_c$  rolls down to the right, i.e., its volume increases without limit; near the top of

the barrier no force acts on the drop and its motion resembles a random walk.

The equation of motion for a single drop in  $r$ -space is

$$\frac{d}{dt} \left( \frac{4\pi}{3} n_0 r^3 \right) = \alpha - \beta, \quad (3)$$

where

$$\alpha = \pi r^2 v_t n$$

is the average frequency of attachment of gas particles to a drop,

$$\beta = \pi r^2 v_t n_s \exp \frac{\gamma}{v^{1/3}}$$

is the evaporation frequency,

$$v_t = \left( \frac{3kT}{m} \right)^{1/2},$$

$m$  is the mass of a gas atom,  $v_t$  is its thermal velocity,  $n$  and  $n_s$  are the density of the gas and of the saturated vapor, respectively,

$$\gamma = \frac{2\sigma}{n_0 kT} \left( \frac{4\pi n_0}{3} \right)^{1/3}$$

is a dimensionless parameter which is  $\sim 10$  and which allows for the surface tension.

If  $r < r_c$ , the right-hand side of Eq. (3) is negative and we consequently have  $dr/dt < 0$ , i.e., any subcritical drop should decrease with time and finally dissociate into single atoms. The random and very unlikely process in which, instead of evaporating, the atoms become attached to one another and create a drop of supercritical size can be described by introducing a function representing the distribution of the nuclei in respect of their size  $g_v$  and subjecting this function to the "master transport equation"<sup>11</sup>

$$\frac{dg_v}{dt} = \alpha_{v-1} g_{v-1} - (\alpha_v + \beta_v) g_v + \beta_{v+1} g_{v+1}. \quad (4)$$

This system of equations represents a special case of a Markov chain in which allowance is made for the transitions of a drop from a state  $v$  to the nearest state with  $v-1$  and  $v+1$  particles.

It is assumed that the chain of equations (4) begins from  $v=2$ , i.e., that drops consisting of  $v > 2$  particles are stable and have properties identical with those of macroscopic drops.

The subsequent treatment is based on the possibility of reducing Eq. (4) to a differential equation, which is done by introducing an "equilibrium" function of the distribution of the size of the nuclei

$$b_v \propto \exp \left( - \frac{\Delta\Phi(v)}{kT} \right),$$

where  $\Delta\Phi(v)$  is described by Eq. (1). Using the function  $b_v$ , we can modify the system of equations (4) by eliminating the coefficient  $\beta$  and thus reduce the system (4) to a second-order differential equation

$$\frac{\partial g}{\partial t} = \frac{\partial j}{\partial v} \equiv \left( D b \frac{\partial}{\partial v} \frac{g}{b} \right), \quad (5)$$

i.e., to an equation of the Fokker-Planck type. In particular, near the top of the barrier where  $b$  is independent of  $v$ , Eq. (5) describes a random walk of a nucleus characterized by  $r = r_c$ .

We shall consider the steady-state situation

( $\partial g / \partial t = 0$ ) when the "flux"  $j$  of drops with any value of  $v$  is constant and independent of time:

$$j = D b \frac{\partial}{\partial v} \frac{g}{b}. \quad (6)$$

The steady states play an important role in the concept of nucleation; actual realization of a steady state requires the presence of drops of macroscopic size: they have to be removed from the system because otherwise the concentration of the liquid will rise without limit. In particular, the Becker-Döring model<sup>11</sup> postulates that drops of supercritical size are removed immediately from the system and split into atoms which then return to the system and maintain a constant density of the gaseous phase. In Sec. 3 we shall see that when drops are really removed from the system, the situation is more complex and more interesting.

We shall now return to Eq. (6) for the flux of particles across a barrier; we can see that the rate of nucleation is governed mainly by the steady-state distribution function  $b$ , which depends exponentially on the degree of supersaturation and has a minimum near the top of the barrier.

Comparing the equation of motion for the average rate of change of the drop size [Eq. (3)] with Eq. (5), we can obtain the "diffusion coefficient"<sup>3)</sup> denoted by  $D$ :

$$D = kT \frac{\alpha - \beta}{d\Phi/dr}.$$

Since near the top of a barrier the motion of a nucleus is almost of a diffusion nature, there is a characteristic time for overcoming a barrier known as the Zel'dovich time  $\tau_Z \approx \Delta v_c^2 / D$ , where  $\Delta v_c$  is a region of size close to  $v_c$  corresponding to a change in the barrier height  $\Delta\Phi$  by  $kT$ .

If the supersaturation is induced abruptly, the transient nucleation rate is

$$\frac{dg}{dt} = \left( \frac{dg}{dt} \right)_{st} \exp \left( - \frac{\tau_Z}{t} \right), \quad (7)$$

where  $\tau_Z$  represents the time for the establishment of the rate of nucleation of nuclei of size in the subcritical region (although the "distance"  $\Delta v \ll v_c$ , the time for the establishment of a quasiequilibrium in a region  $1 < v \lesssim v_c$ , may be short compared with  $\tau_Z$ ).

Further development of the theory (see, for example, Ref. 13) has refined Eq. (7) somewhat, but has not altered the main result which is that in the case of an abrupt supersaturation in the subcritical region a quasiequilibrium distribution is established rapidly (in a time  $\sim \tau_Z$ ) and subsequently the critical region is the source supplying drops of macroscopic size.

### 1.1. Model processes

Steady-state and transient nucleation have been observed clearly in two model situations: in the crystallization of some glasses<sup>14</sup> and in the conversion of an exciton gas into an electron-hole liquid in germanium.<sup>15,16</sup> We shall now describe briefly these model systems.

### 1.2. Glasses

If the temperature is sufficiently low, a metastable glassy state of matter is practically permanent because of the low mobility of atoms. Variation of temperature can ensure any crystallization rate of glass, i.e., it can ensure a transition to the ground state.

Hammel carried out one of the first investigations of the kinetics of crystallization of glass and said<sup>17</sup>: "...Glass-forming systems are ideal for kinetic studies since the studies can be conducted at extremely high viscosities where the mobility of the ions involved in the structural rearrangements accompanying the phase separation is extremely low. Thus direct measurements of transient times and steady-state nucleation rates can be obtained with a minimum of experimental difficulty."

One of the materials investigated by Gutsov *et al.*<sup>18</sup> was a Graham glass in the form of sodium metaphosphate  $\text{NaPO}_3$ . Under normal conditions the crystallization of this glass begins on the surface of a sample, but when salts of some noble metals (for example, Au, Pt, Ag) are added to the melt, the crystallization becomes a bulk process. This process is catalyzed by crystallites of metals which can be detected by dissolving this glass in water.

Kalinina *et al.*<sup>19,20</sup> investigated crystallization of lithium disilicate  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ ; these investigations were normally carried out using the "development" method when crystallites, created at a relatively low temperature, grow at higher temperatures to a visible size.

The ability to extend over hours and days the processes which normally last a fraction of a microsecond is very convenient from the point of view of investigation of the nucleation of crystals in glasses compared with other systems. A shortcoming of such systems is the indeterminacy of the state of the "gaseous" phase; in some cases it is not even clear whether atoms, groups of atoms, or individual bonds become crystallized, so that it is necessary to speak of the crystallization of "kinetic units".<sup>19</sup>

### 1.3. Electron-hole drops

Condensation of excitons into electron-hole (EH) drops was predicted by Keldysh<sup>21</sup> and first detected experimentally by Pokrovskii and Svistunov<sup>22</sup> as well as by Asnin and Rogachev<sup>23</sup> about 20 years ago. Many papers and reviews have been published on this effect.<sup>15,16,24</sup>

When a semiconductor (for example, germanium) is illuminated with an external light source, nonequilibrium electrons and holes created in a sample are bound (by the Coulomb interaction) at low temperatures into excitons, i.e., into quasi-atoms which move freely along a crystal. When these excitons reach a sufficiently high density, they condense (like atoms of conventional gases) into bunches of a dense degenerate EH plasma (EH drops). All the geometric and energy scales typical of EH drops are different from those of conventional condensed substances and this is due to two reasons: firstly, the Coulomb interaction between the charges is reduced by a factor of  $\kappa$  (where  $\kappa$  is the permittivity of the crystal); secondly, the effective mass  $m^*$  of carriers is usually several times smaller than the mass of a free electron. Therefore, the Bohr radius of an indirect exciton  $a_0 = \kappa \hbar^2 / m^* e^2$  in Ge amounts to

$$a_0 \approx 10^{-6} \text{ cm},$$

and not to  $\sim 10^{-8}$  cm as in the case of the hydrogen atom. Consequently, the binding energy of an exciton

$$\varepsilon_{\text{ex}} = \frac{m^* e^4}{2\kappa^2 \hbar^2}$$

represents a few millielectron-volts (for example, in the case

of germanium we have  $\varepsilon_{\text{ex}} \approx 4$  meV), which is the reason why most of the experiments have been carried out at liquid helium temperatures.

The easiest and most informative method for the determination of the parameters of an EH liquid is a study of its recombination radiation (luminescence).<sup>22</sup> The spectrum of recombination radiation emitted by Ge is shown in Fig. 2: the main lines in the spectrum correspond to an EH liquid (with a maximum at 709 meV) and excitons (713 meV). The luminescence is due to radiative recombination of an electron and a hole; since electrons and holes fill Fermi spheres characterized by energies  $\varepsilon_{\text{Fc}}$  and  $\varepsilon_{\text{Fh}}$ , the short-wavelength edge of a luminescence line corresponds to the chemical potential. These data yield the equilibrium density of the liquid which is  $n_0 \approx 2.4 \times 10^{17} \text{ cm}^{-3}$ . Figure 2 includes also the binding energy of an EH liquid  $\varphi_0 = 2$  meV and the binding energy of an exciton  $\varepsilon_{\text{ex}} \approx 4$  meV.

Recombination in a drop is mainly due to Auger processes when the energy of a recombining pair is transferred to a third body (electron); therefore, the drop lifetime  $\tau_0 \approx 40 \mu\text{s}$  is a universal characteristic of the EH liquid in Ge.

The ratio of the lifetime of particles in an EH liquid to the relaxation time of their energy is high ( $\approx 10^4$ ), so that the state of the liquid can be regarded as quasiequilibrium.

The growth and dissociation of an individual drop can be described by an equation analogous to Eq. (3):

$$\frac{d}{dt} \left( \frac{4\pi}{3} n_0 r^3 \right) = \pi r^2 v_i [n - n_s(r)] - \frac{4\pi}{3\tau_0} n_0 r^3, \quad (8)$$

where  $n_s(r) = n_s \exp(2\sigma/n_0 kT)$  is the saturated vapor density above a drop of radius  $r$ . The second term on the right-hand side of Eq. (8) is due to the finite lifetime of a drop. The important difference between Eqs. (8) and (3) is the possibility of formation of a stable steady state of EH drops. Under steady-state conditions, when the volume of a drop is independent of time, we have

$$n = n_s \exp \frac{2\sigma}{n_0 kT r} + \frac{4n_0 r}{3v_i \tau_0}. \quad (9)$$

The first term in Eq. (9) is the saturated vapor density above a drop of radius  $r$  and it is not related to the specific properties of an EH liquid, whereas the second term is due to the

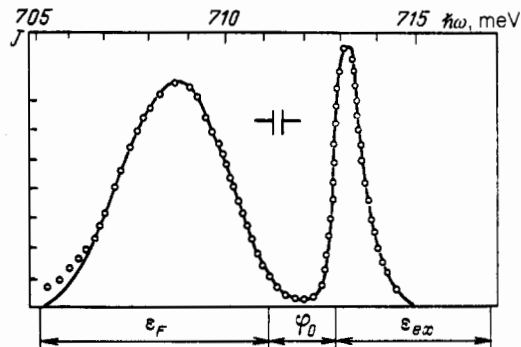


FIG. 2. Luminescence spectrum of Ge demonstrating the results of an analysis of the profile of the line representing the LA phonon replica of an electron-hole liquid and of excitons.<sup>25</sup>  $T = 3.5$  K. The experimental results are represented by circles. Here,  $\varepsilon_{\text{ex}}$  is the binding energy of an exciton,  $\varepsilon_{\text{F}}$  is the total Fermi energy of electrons and holes in an electron-hole liquid, and  $\varphi_0$  is the binding energy per pair of particles in an electron-hole liquid.

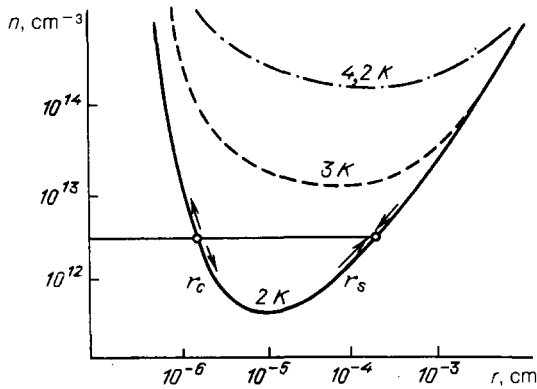


FIG. 3. Dependence of the density of excitons on the drop radius under steady-state conditions [see Eq. (9)]. Here,  $r_c$  is the radius of a stable drop and  $r_s$  is the radius of a critical nucleus.

finite lifetime  $\tau_0$  of the liquid and it increases on increase in  $r$  and on reduction in  $\tau_0$ .

It follows from Eqs. (8) and (9) that, in contrast to equilibrium systems, conservation of a given drop size requires continuous inflow of matter from outside. The rate of internal recombination is proportional to the volume of a drop (to  $r^3$ ), whereas the flux reaching a drop is proportional to its surface (to  $r^2$ ). Therefore, for any gas density there is a size for which the rate of bulk recombination balances out the inflow of matter.

Therefore, the function  $n(r)$  has two branches (Fig. 3): a falling branch which represents the dependence of the saturated vapor density on the drop radius and a rising branch due to the nonequilibrium of the liquid. The straight line parallel to the  $r$  axis may intersect the graph of  $n(r)$  at two points  $r_c$  and  $r_s$ , which are equilibrium points. At the left-hand point  $r_c$  the equilibrium is unstable: a change in the drop radius by a small amount  $\delta r$  generates a deviation which continues to rise until the system reaches the point  $r_s$ , which is stable, or until the drop evaporates completely ( $r \rightarrow 0$ ). The left-hand branch of  $n(r)$  represents a family of critical nuclei, whereas the right-hand branch corresponds to stable drops. For  $n = n_{\min}(T)$ , the values of  $r_c$  and  $r_s$  merge to form a point  $r_{\min}(T)$ :

$$r_{\min} \approx \frac{1}{n_0} \left( \frac{6\sigma\tau_0\nu_\tau n_0}{kT} \right)^{1/2}.$$

Clearly, the minimum exciton density at which a liquid can exist is higher than  $n_s$  and it increases on reduction in the liquid lifetime.

The kinetics of nucleation of an EH liquid is governed by Eq. (4) where the coefficient  $\beta_\nu$  should be written in the form

$$\beta_\nu = \pi r^2 \nu_i n_s \exp \left( \frac{2\sigma}{n_0 r kT} \right) + \frac{\nu}{\tau_0},$$

which makes it possible to allow for the  $(\nu + 1) \rightarrow \nu$ , and  $\nu \rightarrow (\nu - 1)$  transitions due to recombination of particles inside a drop. This gives rise to an additional term in the "quasi-thermodynamic potential"<sup>26,27</sup>:

$$\Delta\psi(\nu) = -\nu kT \ln \frac{n}{n_0} + 4\pi\sigma r^2 + \sum_{i=2}^{\infty} kT \ln \left( 1 + \frac{1}{\alpha_i \tau_0} \right), \quad (10)$$

where the first two terms are identical with Eq. (1) and the

last term, related to the finite lifetime, induces an abrupt termination of the function representing the distribution of the drop sizes in the range  $r \gtrsim r_s$ .

It therefore follows that an important advantage of a transition from excitons to an EH liquid over other first-order phase transitions is that the size of the resultant drop is limited and the total concentration of the liquid is linked uniquely to the number of nucleation events. Another advantage is that Ge crystals can be very pure and can have very few defects, so that the nucleation process is homogeneous. Finally, a change in the conditions for the appearance of a liquid is achieved by a simple change in the time profile of exciting light pulses.

Supersaturation of an exciton gas was discovered by Lo, Feldman, and Jeffries<sup>28</sup> in pure samples of Ge with no more than  $10^{11} \text{ cm}^{-3}$  of impurities. Supersaturation gave rise to a hysteresis of the intensity of the luminescence emitted by a system of excitons and EH drops near the liquid formation threshold (Fig. 4). When the rate of pumping  $G$  of a sample was gradually increased and then reduced, the threshold of appearance of a liquid  $G_+$  exceeded the threshold of disappearance  $G_-$  (Fig. 4); the ratio  $G_+/G_-$  was related (bearing in mind the finite lifetime of a drop) to the degree of supersaturation of an exciton gas at the condensation threshold.

Westervelt<sup>29</sup> measured the characteristic metastable time of such a system, i.e., the time for disappearance of hysteresis; it was found that this time could reach  $\sim 10^5$  s; therefore, this nonequilibrium system "retained the memory" for  $\sim 10^9$  generations of electrons and holes forming the system.

The theory of nucleation agrees with the experimental results if we assume that the drops have a surface tension of  $\sigma \approx 2.6 \times 10^{-4} \text{ erg/cm}^2$ , which is in good agreement both with calculations<sup>30</sup> and with an elementary estimate<sup>1</sup>

$$4\pi\sigma \left( \frac{3}{4\pi n_0} \right)^{2/3} = \varphi_0,$$

in which the surface energy of a unit cell is equated to the binding energy. Fuller details can be found in Westervelt's review.<sup>31</sup>

## 2. STEADY-STATE AND TRANSIENT NUCLEATION

We shall consider a condensing gas the supersaturation of which depends on time (i.e., we shall bear in mind that the coefficients  $\alpha$  and  $\beta$  of the master transport equation can be functions of  $\nu$  and  $t$ ). The simplest transient case represents an abrupt appearance of supersaturation at  $t = 0$  and it is considered in Ref. 12. The time interval  $\tau_Z$  necessary for the establishment of a steady-state nucleation rate is then de-

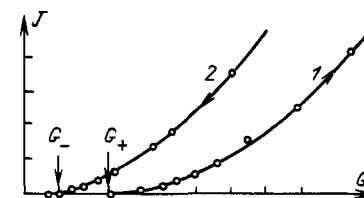


FIG. 4. Hysteretic dependence of the intensity of the luminescence  $J$  on the rate of pumping  $G$  obtained for Ge (Ref. 28): 1) rising branch with a threshold  $G_+$ ; 2) falling branch with a threshold  $G_-$ .

finied by Eq. (7) and it corresponds to the establishment of a steady-state flux of supercritical nuclei in the space of the drop dimensions.

The steady-state nucleation rate can be calculated using Eq. (6) for the flux of drops along the axis of drop dimensions:

$$j = Db \frac{\partial}{\partial v} \frac{g}{b}, \quad g = \frac{b}{D} \int \frac{j}{b} dv \approx \frac{j b}{D} \int \frac{dv}{b}. \quad (11)$$

The integrand in Eq. (11) has a sharp maximum near the critical drop size  $r_c$ ; following Ref. 12, i.e., expanding  $\Delta\Phi$  as a series, we readily obtain the final expression for the flux of the newly created drops:

$$j = D_c b_c \left( -\frac{1}{2\pi kT} \frac{\partial^2 \Delta\Phi}{\partial v^2} \right)^{1/2} \\ = \left( -\frac{1}{2\pi kT} \frac{\partial^2 \Delta\Phi}{\partial v^2} \right)^{1/2} D_c n \exp \left( -\frac{\Delta\Phi_{\max}}{kT} \right).$$

We can thus see that in the case of steady-state nucleation in the subcritical region a near-equilibrium distribution of the sizes of the nuclei is established. The deviation from equilibrium is small and it is important only near  $r = r_c$ .

In the case of the transient problem we must stress that at present we do not know the exact solution of Eq. (5) and particularly of the master transport equation [Eq. (4)]. The role of transient effects (Fig. 5) can be described qualitatively as establishment of a quasiequilibrium in the range  $r < r_c$  in a characteristic time  $t_c$  and the establishment in a time  $\tau_Z$  of a diffusion flux across the top of the barrier. The sum of these times is the total delay time. We shall show later that we usually have  $t_c < \tau_Z$ , so that in fact the total delay time is equal to  $\tau_Z$ . This can be demonstrated by going over from Eq. (4) to a differential equation

$$\frac{\partial g}{\partial t} = \frac{\partial}{\partial v} [(\beta - \alpha) g] + \frac{\partial^2}{\partial v^2} \left( \frac{\alpha + \beta}{2} g \right). \quad (12)$$

This equation is suitable for the description of the motion of a system over short distances along the  $v$  axis. Far from equilibrium points ( $\beta = \alpha$ ) Eq. (12) reduces to a first-order equation

$$\frac{\partial g}{\partial t} = \frac{\partial}{\partial v} [(\beta - \alpha) g],$$

i.e., the equation for the drift of an arbitrary perturbation with a natural scale of time  $(\beta - \alpha)^{-1}$ . Consequently, the time taken by a nucleus to travel from the top of the barrier to  $v = 1$  is

$$t_c \approx \int_1^{v_c - \Delta v} \frac{dv}{\beta - \alpha}. \quad (13)$$

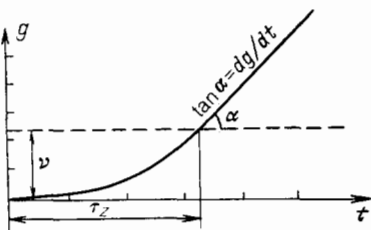


FIG. 5. Time dependence of the total number of newly formed drops.<sup>12</sup> The initial part demonstrates the role of transient nucleation and  $\tau_Z$  is the Zel'dovich time.

The upper limit of the integral in Eq. (13) is shifted to the left from the top of the barrier by a distance  $\Delta v$ . Equation (13) has the simple meaning of the time for a nucleus to roll down from the top of the potential barrier (Fig. 1) if initially this nucleus is on the left-hand slope near the top.

If  $v \approx v_c$ , the "diffusion" and "drift" terms should be included in Eq. (12) as of equal importance. We shall now adopt dimensionless variables

$$x = (v - v_c) \left[ \frac{1}{2\alpha_c} \left( \frac{d\alpha}{dv} - \frac{d\beta}{dv} \right) \right]^{1/2}, \quad \zeta = \frac{t}{2} \left( \frac{d\alpha}{dv} - \frac{d\beta}{dv} \right),$$

where  $\alpha_c = \beta_c$  is the frequency of attachment of atoms to a critical nucleus, equal to the loss frequency; then Eq. (12) becomes

$$\frac{\partial g}{\partial \zeta} = \frac{\partial^2 g}{\partial x^2} - 2x \frac{\partial g}{\partial x} - 2g.$$

Clearly, a "distance"  $x \approx 1$  is traveled by a particle in a "time"  $\zeta \approx 1$ . Consequently,  $\Delta v$  is of the order of

$$\Delta v = v - v_c \approx \left[ 2\alpha_c \left( \frac{d\alpha}{dv} - \frac{d\beta}{dv} \right)^{-1} \right]^{1/2},$$

and the diffusion-drift time near the top of the barrier is

$$t_2 \approx 2 \left( \frac{d\alpha}{dv} - \frac{d\beta}{dv} \right)^{-1}.$$

The "distance"  $\Delta v$  and the time  $t_2$  are related by the "diffusion" equation

$$t_2 = \frac{\delta^2}{\alpha_c}.$$

Direct calculations readily show that the quantity  $t_2$  is functionally identical with the time  $\tau_Z$  (numerically the relationship is  $t_2 = 2\tau_Z$ ) and exceeds by approximately an order of magnitude the value of  $t_c$  for realistic degrees of supersaturation. Therefore, the time for the establishment of a steady-state nucleation rate is approximately equal to the time for a random walk of a nucleus near the top of the barrier.

The solution described by Eq. (7) describes qualitatively the "diffusion" limit; several investigations have been made in order to refine this limit (see, for example, Refs. 32-34). A transient current is described in Ref. 34 by

$$j(t) \propto 1 + 2 \sum_{k=1}^{\infty} (-1)^k \exp \left( -\frac{k^2 t}{\tau} \right);$$

this slowly converging series can be transformed to another series

$$j(t) \propto \sum_{m=1}^{\infty} \exp \left[ -\frac{\tau}{(2m-1)^2 t} \right],$$

where the first term is identical with the result given by Eq. (7). Equation (7), which is identical with the expression for unlimited one-dimensional diffusion from a point source, is the most reliable one for a comparison with the experimental results.

If the coefficients in Eq. (3) are more complex functions of time, then the behavior of the system cannot be predicted easily even in the qualitative sense, but this is subject to one exception: if the characteristic time for the changes in  $\alpha$  and  $\beta$  is long compared with  $\tau_Z$ , we might expect the process to be quasisteady<sup>35</sup> so that a flux of nuclei with supercritical and critical size adjusts itself to the barrier configuration which varies with time. In particular, an increase in the amount of the condensed phase for a constant total number

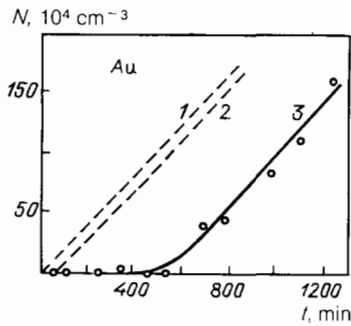


FIG. 6. Dependence of the concentration of Au microcrystals in ( $\text{NaPO}_3$ )<sub>x</sub> glass on the duration of treatment<sup>18</sup>: 1) without allowance for the delay time; 2) allowing for the time taken to grow to the experimentally observed size; 3) experimental results.

of particles in the system reduces the degree of supersaturation; therefore, a dependence of the type shown in Fig. 5 can be observed only during the initial stage of the condensation process.

In a comparison with the experimental results it should be noted that in experiments it is important to distinguish an increase in the number of nucleation events from an increase in the volume of the new phase. Such a distinction is indeed observed in the processes of crystallization of glasses and formation of EH drops.

### 2.1. Glasses

In the case of glasses the qualitative agreement between the theory and experiment is very striking. Figure 6 shows the dependence of the concentration of microcrystals of gold in glassy sodium metaphosphate on the duration of treatment<sup>18</sup> and Fig. 7 gives the corresponding dependence for crystallites in lithium disilicate.<sup>20</sup> Clearly, in both cases there is a time interval during which the nucleation rate (equal to the slope of a tangent touching the graphs in Figs. 6 and 7) is very small and then the nucleation rate rises and after a time the process becomes steady-state. The dashed straight lines in Fig. 6 show the dependence  $n(t)$  which would be obtained in the absence of a delay time (line 1) and after allowance for the necessary time taken by a nucleus to reach the minimum visually detectable size (line 2). The rate of nucleation depends exponentially on temperature in both cases (Figs. 6 and 7); the absolute value of the nuclea-

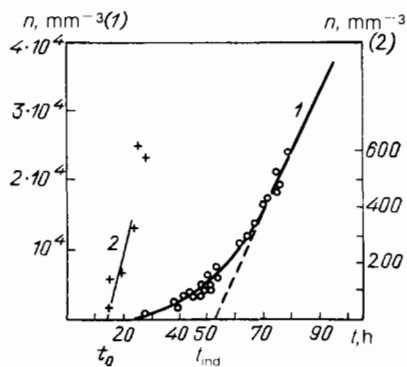


FIG. 7. Dependence of the concentration of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  spherulites on the duration of treatment of glass of the same composition<sup>19</sup> (1) and the initial part of curve 1 shown on an enlarged scale (2).

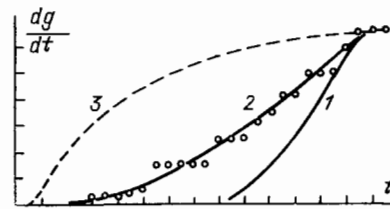


FIG. 8. Dependence of the rate of nucleation on the duration of treatment of glass found by graphical differentiation of Fig. 6 (curve 1) and of Fig. 7 (curve 2). Curve 3 is plotted on the basis of Eq. (7).

tion rate can be explained by means of formulas such as Eqs. (10) and (7). It is demonstrated in detail in Refs. 18 and 20 that the nonlinear parts of these dependences are due to transient nucleation. There is no doubt about the correctness of this conclusion; however, if the problem is considered in greater detail, a comparison of the rate of nucleation found by graphical differentiation of the curves in Fig. 6 with the result given by Eq. (7) demonstrates that the agreement is not so good (Fig. 8).

We shall consider briefly the experiments on crystallization of glass at a temperature  $T_2$  after a preliminary heat treatment at a temperature  $T_1 < T_2$  (Ref. 36), which demonstrated that during the transient interval the nucleation rate is anomalously high (Fig. 9). The results plotted in Fig. 7 can be explained if we allow for the explicit dependences of the rates of growth  $\alpha$  and dissociation  $\beta$  on the size of a nucleus. This dependence can be due to structural relaxation of atoms or groups of atoms in glass as a result of a change in temperature, i.e., it may be due to the glass stabilization effect.<sup>37</sup> As a result of such stabilization the configuration of a thermodynamic barrier of Eq. (1) depends on time: the barrier may be established rapidly in the case of low values of  $\nu$  and slowly in the case of high values of this parameter. The time dependence of the barrier may in principle explain the disagreement between the data plotted in Figs. 8 and 9, on the one hand, and the "diffusion" model of Eq. (7).

Behavior which was much less pronounced but still analogous to that in Fig. 9 had been observed also in the crystallization of glasses of a different composition.<sup>20</sup> It should be noted that if the above hypothesis proves to be correct, experiments of the type for which the results are plotted in Figs. 6 and 7 may be used to study the kinetics of stabilization of glass.

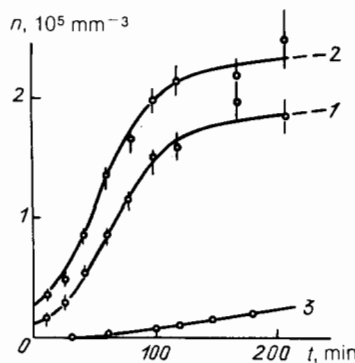


FIG. 9. Dependence of the number of nuclei on the duration of treatment at  $T_2 = 465^\circ\text{C}$  obtained for  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  glass subjected to a preliminary treatment at  $T_1$  for a time  $t_1$  (Ref. 36): 1)  $T_1 = 430^\circ\text{C}$ ,  $t_1 = 65$  h; 2)  $T_1 = 430^\circ\text{C}$ ,  $t_1 = 89$  h; 3) quenched glass.

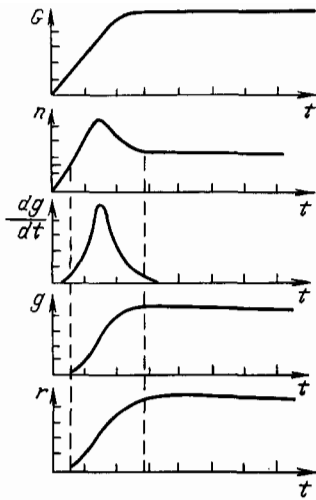


FIG. 10. Quasisteady kinetics of nucleation of electron-hole drops.<sup>40</sup> Here,  $G$  is the rate of external pumping,  $n$  is the exciton density,  $dg/dt$  is the rate of nucleation,  $g$  is the concentration of drops, and  $r$  is the drop radius.

## 2.2. Electron-hole liquid

In a system of excitons and of an EH liquid in Ge the simplest method for the observation of the transient effects involves pulsed illumination of a sample. If an external pumping rate  $G$  initially rises slowly, and then stabilizes (Fig. 10), it follows that the nucleation of a liquid is a quasisteady process.<sup>38</sup>

The size of the drops, their concentration, and the exciton density are described by Eq. (3) and by

$$\frac{dn}{dt} = G(t) - \sum_v \pi r_v^2 v_i (n - n_s(r)) g_v - \frac{n}{\tau}. \quad (14)$$

The density of excitons described by Eq. (14) increases as long as the loss of excitons from a drop can be ignored. When the necessary degree of supersaturation is achieved, the rate of nucleation  $dg/dt$  begins to fall rapidly; however, as long as the total surface of the drops which are formed is small in spite of the high concentration of nuclei, the exciton density continues to rise. When the size of the drops formed in this way is sufficiently large (i.e., when these drops grow from the critical to the stable size, which requires a time  $\sim \tau_0$ ), the exciton density and consequently the nucleation rate fall. Relaxation of the system then reduces to the growth of drops and reduction in the exciton density. Staehli<sup>39</sup> excited a sample of pure Ge with light pulses characterized by a rise time of  $\sim 10 \mu\text{s}$ ; however, a nonmonotonic time dependence of the exciton density was not observed; according to the author, this was due to a spatial inhomogeneity of the system. A qualitative agreement with Fig. 9 was achieved in Ref. 38, where the light scattering method was used to determine the concentration and size of the droplets generated in a sample using excitation fronts of different steepness, and it was found that in the case of a steep front many small droplets were excited, whereas in the case of a slow rise the number of droplets was small but they were large.

An initial nonequilibrium of the gaseous phase was used in Refs. 40 and 41 to determine the steady-state and transient rates of nucleation of an EH liquid. A sample was subjected to a microwave field which heated nonequilibrium carriers and increased their density; consequently, the nucleation

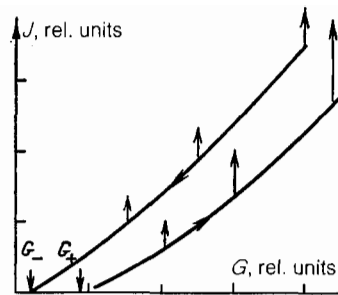


FIG. 11. Influence of a heating microwave field on the luminescence emitted by an electron-hole liquid.<sup>41</sup>

threshold was shifted toward higher pumping rates. The heating of nonequilibrium carriers affected the nucleation rate, but had practically no effect on macroscopic drops. Therefore, if a field was applied to a sample in which drops were created in advance (Fig. 11), the number of drops was not affected and their size increased slightly because of an increase in the total flux of matter from the gaseous phase. However, when a field was applied first and then the pumping was increased, the nucleation threshold increased (particularly in the case of a pure sample, as shown in Fig. 12) because of nonisothermal conditions for the nucleation and removal of nuclei from the excitation region.<sup>4)</sup>

Figure 13 shows schematically the method used to determine the nucleation rate<sup>40</sup> when the heating field was switched off for a time  $\theta$  and the period of such switching was  $T_0$ . In the range  $\theta \gg \tau_z$  the nucleation was quasisteady for a time  $\theta$ ; during the rest of the period ( $T_0 - \theta$ ) new drops were not formed and the old ones did not yet disappear (lower curve in Fig. 13). It should be noted that in the case of this measurement method the detailed mechanism of the effect of a microwave field on the process of nucleation is unimportant; the only significant point is that the time for the change in the system to the initial "cold" state is less than  $\tau_z$ .

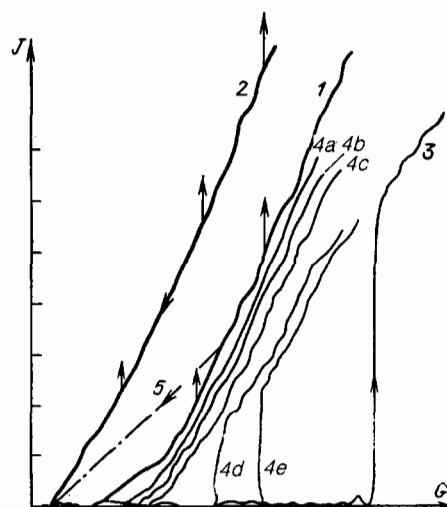


FIG. 12. Dependences of the intensity of the luminescence emitted by electron-hole drops on the external pumping rate  $G$  (Ref. 40): 1), 2) rising and falling branches in the absence of a microwave field; 3), 5) same branches in the presence of a microwave field of  $E \approx 30 \text{ V/cm}$  intensity; 4) rising branch of  $J(G)$  obtained in a field  $E \approx 30 \text{ V/cm}$  by varying the duration of field pulses  $\theta$ : 4a)  $\theta = 10^{-3} \text{ s}$ ; 4b)  $\theta = 10^{-4} \text{ s}$ ; 4c)  $\theta = 10^{-5} \text{ s}$ ; 4d)  $\theta = 10^{-6} \text{ s}$ ; 4e)  $\theta = 4 \times 10^{-7} \text{ s}$ .



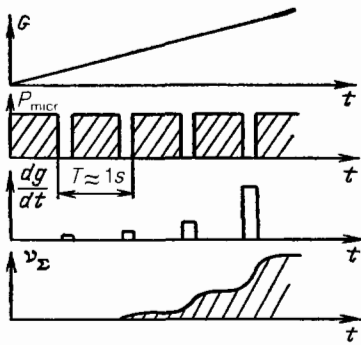


FIG. 13. Schematic representation of the determination of the nucleation rate.<sup>40</sup> Here,  $G$  is the rate of external pumping;  $P_{\text{micr}}$  is the microwave field power;  $dg/dt$  is the rate of condensation;  $v_{\Sigma} = (4\pi/3)n_0 r^3 g$  is the total amount of the liquid.

The smaller the value of  $\theta$  the higher the threshold for the appearance of a liquid (curves a–e in Fig. 12). Figure 14 shows the results of a comparison of the experimental data with a theory of steady-state nucleation: when plotted in the form of the dependence  $\ln \theta^{-1} = f[\ln^{-2}(n/n_s)]$  the experimental points fit straight lines with the slope that governs the surface tension. In the range  $\theta = 1-10^{-5}$  s the kinetics of formation of an EH liquid is described satisfactorily by the steady-state theory of nucleation. Using Eq. (1'), we can estimate the number of electron-hole pairs in a critical nucleus  $\nu_c$  which would change in a time  $15 \lesssim \nu_c \lesssim 30$  and one can then draw the conclusion that such a nucleus has a binding energy and surface tension close to the corresponding macroscopic values.

When  $\theta$  is reduced to  $\sim 10^{-6}$  s, the dependences shown in Fig. 14 differ from the theoretical curves; the difference is such that in a comparison of a small increase in the rate of nucleation one would require a considerable increase in the degree of supersaturation. It would seem natural to relate this effect to the appearance of transient nucleation. The pure form of such nucleation was observed employing a heating microwave field which was modulated by pulses with an off-duty factor of 2 and a period  $T_0 = 2\theta = 10^{-3} - 5 \times 10^{-7}$  s (Ref. 41). In contrast to the diagram shown in Fig. 13, the value of  $T_0$  varied from one experiment to another within a wide range, but the time allowed for condensation was independent of the modulation frequency and re-

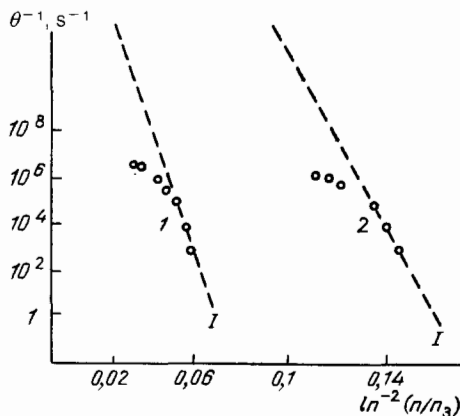


FIG. 14. Dependence of the condensation rate  $dg/dt \propto \theta^{-1}$  on the degree of supersaturation<sup>40</sup>: 1)  $T = 1.53$  K; 2)  $T = 1.85$  K.

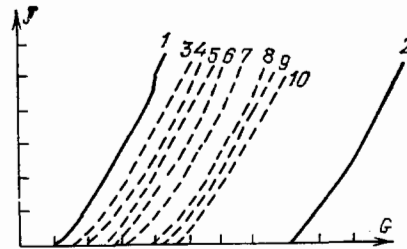


FIG. 15. Metastable branch of  $J(G)$  obtained using different methods of application of a microwave field (transient nucleation)<sup>41</sup>: 1) no heating field; 2) field applied continuously; 3)–10) field pulses of duration equal to half the period,  $f\theta = 1/2$ ; 3)  $f = 0.1$  MHz; 4)  $f = 0.2$  MHz; 5)  $f = 0.3$  MHz; 6)  $f = 0.4$  MHz; 7)  $f = 0.6$  MHz; 8)  $f = 0.8$  MHz; 9)  $f = 1.0$  MHz; 10)  $f = 2.0$  MHz.  $T = 1.65$  K.

mained equal to  $T_0/2$ , i.e., it should be half of the value in the absence of the field. Therefore, if the nucleation had been steady-state at all values of  $T_0$  the nucleation threshold would have been independent of the modulation frequency. This was found to be true as long as the modulation frequency  $f = 1/T_0$  did not exceed 50 kHz (Fig. 15). Curve 1 in Fig. 15 represents  $J(G)$  in zero microwave field as well as in microwave fields modulated at frequencies from 1 to 50 kHz. Curve 2 is the dependence  $J(G)$  in an unmodulated microwave field. In the range  $f > 100$  kHz a shift of the nucleation threshold toward higher pumping rates was observed (curves 3–8) and this was due to the transient nature of the process, i.e., it was due to the fact that in the case of instantaneous appearance of supersaturation the function representing the size distribution of the nuclei was established in a finite time  $\tau_z$  estimated above.

When the field was switched off, the barrier hindering nucleation decreased and the nuclei "diffused counter to the field" to the supercritical region after a characteristic time  $\tau_z$ . The application of a field increased the barrier height because of an increase in the critical size, the nuclei which would have been supercritical in the absence of the field were then found to be subcritical, i.e., they evaporated rapidly in a time  $t_c \ll \tau_z$ . We could therefore assume that in the case of periodic application of a field the process of establishment of the distribution function occurred in the same way as in the case of appearance of supersaturation in the form of a single step. In comparing the theory with the experimental results we shall introduce into Eq. (13') the experimentally determined quantities:

$$\tau_z = \frac{8\sigma}{nkTv_s \ln^2(n/n_s)} \quad (15)$$

Taking the logarithms of Eq. (15) and substituting  $f = 1/\tau_z$  we obtain

$$b = \frac{af}{n} + \ln^2 \frac{n}{n_s}, \quad (16)$$

where  $a$  and  $b$  are constants of suitable dimensionality.

The experimental results are compared in Fig. 16 with Eq. (16); we can see that the experimental points fit a straight line well right up to  $f = 1$  MHz, which is evidence of the validity of the "diffusion" relationship given by Eq. (13'). The experimental value of  $\tau_z$  deduced from the data in Figs. 14 and 15 is  $\tau_z \approx 5 \times 10^{-6}$  s, which is close to the estimate  $\tau_z \sim 10^{-6}$  s, obtained from Eq. (15).

We shall conclude this section by noting that it would

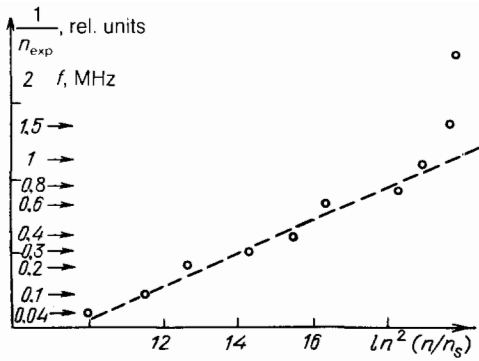


FIG. 16. Comparison of the experimental results of Fig. 15 with the theoretical expression (16). The horizontal arrows identify the modulation frequencies of the microwave field.

be interesting to detect effects associated with transient nucleation of the new phase when the parental medium is in the solid state. In particular it is not clear whether one could speak of fracture of a solid as boiling of a very viscous liquid.<sup>12,59</sup>

### 3. STEADY-STATE NUCLEATION IN AN OPEN SYSTEM. KINETIC BRANCH OF A PHASE TRANSITION

A model of the nucleation process described in the preceding sections reduces to the fact that in the space of drop dimensions there is a "box" containing drops of subcritical size. The walls of this box are almost impermeable, so that the flux of supercritical nuclei is negligible and subcritical drops are in quasiequilibrium. This approach is suitable in the case of slow processes; however, there are cases when such a quasithermodynamic description is not possible and this is true, in particular, of nucleation of a liquid in an open system when drops can escape as a result of diffusion or drift in an external field.

Transition from excitons to EH drops considered from this point of view has a number of advantages over other first-order transitions. These advantages are due to the finite lifetime of the liquid and the mobility of EH drops. The finite lifetime limits the size of a drop (as mentioned above) and makes possible zero-barrier nucleation. The possibility of motion of EH drops relative to the lattice of a crystal makes it possible to reformulate the problem of homogeneous and heterogeneous nucleation, and to realize a steady state in which the nucleation of drops is compensated by their loss from the excitation region (i.e., almost the same as in the case of condensation in an expanding jet,<sup>2</sup> but the problem is isothermal and not adiabatic).

If the nuclei of a liquid phase can be removed rapidly from the region where they are created, which can be due to diffusion or drift in an external field, then (as shown below) the behavior of the system differs considerably from quasiequilibrium. The loss of nuclei from a sample makes it necessary to increase the exciton density, so that near the nucleation threshold the degree of supersaturation of the exciton gas may reach very high values (up to  $10^3$ ). In the case of such supersaturation the thermodynamic Gibbs barrier is found to be small compared with the "kinetic" barrier which is due to the finite growth time of a drop.

It therefore follows that the concept of the condensation threshold corresponding to the maximum supersaturat-

ed vapor density, depending only on temperature, has a limited range of validity.

We shall now consider the steady-state case when drops are nucleated and grow, i.e., when they move in the space of dimensions, whereas in practice they move in real space and leave in a time  $\theta$  a zone in which nucleation and maintenance of liquid drops is possible. The corresponding distribution function of the drop size is the solution of the equation<sup>45</sup>

$$\alpha_{v-1}g_{v-1} - (\alpha_v + \beta_v)g_v + \beta_{v+1}g_{v+1} - \frac{g_v}{\theta_v} = 0. \quad (17)$$

Equation (17) contains a term  $g_v/\theta_v$ , which allows for the diffusion or drift of drops. In the case of drift the time  $\theta$  is independent of  $v$ ; in the case of diffusion<sup>45,46</sup> we have  $\theta_v = d^2/D_v$ , where  $d$  is the thickness of the sample,  $D_v = D_1/v$ , and  $D_1$  is the diffusion coefficient per pair of particles in a drop.

We shall seek the solution of Eq. (17) by methods similar to the WKB approximation<sup>47</sup>:

$$g_v = \exp(-\psi_v), \quad (18)$$

$$g_{v\pm 1} \approx \exp\left(-\psi_v \mp \frac{d\psi}{dv}\right).$$

Substituting Eq. (18) into Eq. (17), we obtain a quadratic equation for  $x = \exp(d\psi/dv)$ :

$$x^2 - (1+a+b)x + a = 0, \quad (19)$$

where  $a = (\beta/\alpha)$  and  $b = (1/\alpha\theta)$ ; however, no allowance is made for the difference between  $\alpha_v$  and  $\alpha_{v-2}$  or between  $\beta_v$  and  $\beta_{v+1}$ . Solving Eq. (19), we obtain

$$\frac{d\psi}{dv} = \ln \left\{ \frac{1+a+b}{2} + \left[ \left( \frac{1+a+b}{2} \right)^2 - a \right]^{1/2} \right\}, \quad (20)$$

$$g = n \exp\left(-\int_1^v \frac{d\psi}{dv} dv\right), \quad (21)$$

where the preexponential term is governed by the exciton density ( $g_1 = n$ ) and the positive sign in front of the root is selected in order to satisfy the boundary condition  $g \rightarrow 0$  for  $v \rightarrow \infty$ .

An important advantage of the approach in which an analysis is made not of the differential Equation (5) or (12), but of the initial finite difference Equation (4) or (17) is the fact that in the latter case we can readily obtain the equilibrium (limiting) distribution function. In fact, if we assume that  $\theta \rightarrow \infty$  ( $b \rightarrow 0$ ), i.e., in the case when hardly any drops leave the system, we find from Eq. (20) that

$$\frac{d\psi}{dv} = \ln a \equiv \ln \frac{\beta}{\alpha}, \quad (22)$$

so that the substitution in Eq. (21) gives

$$\psi = -v \ln \frac{n}{n_s} + \frac{4\pi\sigma r^2}{kT} + \int_1^v \ln [1 + (\alpha\tau_0)^{-1}] dv,$$

i.e., it gives Eq. (10) derived earlier in Ref. 27 by means of complex considerations.

The resultant form of the potential  $\Delta\Phi(r)$  obtained for different degrees of supersaturation is demonstrated in Fig. 17.

Extrema of the function  $\Delta\Phi(r)$  correspond to the critical  $[\Delta\Phi_{\max}(r_c)]$  and stable  $\Delta\Phi_{\min}(r_s)$  dimensions (Fig. 3).

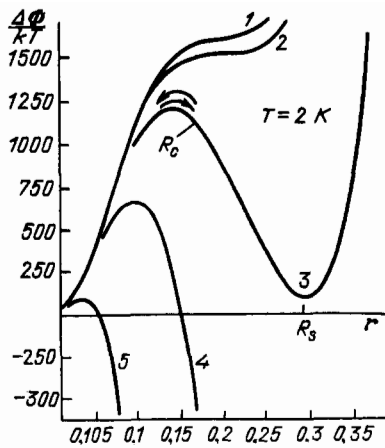


FIG. 17. Difference between the generalized thermodynamic potentials obtained for different degrees of supersaturation<sup>27</sup>  $n/n_s$ : 1) 2.07; 2) 2.08; 3) 2.16; 4) 2.49; 5) 7.46.

We shall continue the mechanical analogy used in the discussion of Fig. 1: small drops are "confined" to the subcritical region and the critical drops that have leaked randomly across a barrier drop into a well near  $r = r_s$  and accumulate there. We must remember that Eq. (22) is an equilibrium function corresponding to a negligibly small flux of drops at any value of  $v$ . Therefore, if we try to compare the "potential" of Eq. (10) with the distribution function of Eq. (21), we find that enormous concentrations of macroscopic drops should form (which is true, for example, of curves 4 and 5 in Fig. 17), which is physically meaningless.

An important exception to this rule is the case of low temperatures, when supersaturation is very high, there is no hysteresis near the nucleation threshold, and curves of the type labeled 1 and 2 in Fig. 17 describe the actually observed states. At low temperatures the thermodynamic barrier hindering nucleation practically disappears. However, the process of recombination in a drop requires a certain rate of arrival of matter from outside, from the gaseous phase, so that the density of the surrounding gas should be finite and almost independent of temperature in order to maintain a drop. Turning to Fig. 4 we can see that in this case the points  $r_c$ ,  $r_s$ , and  $r_{min}$  merge because the exciton density  $n_{min}$  ensures the required nucleation rate and maintains stable drops of the minimum size.

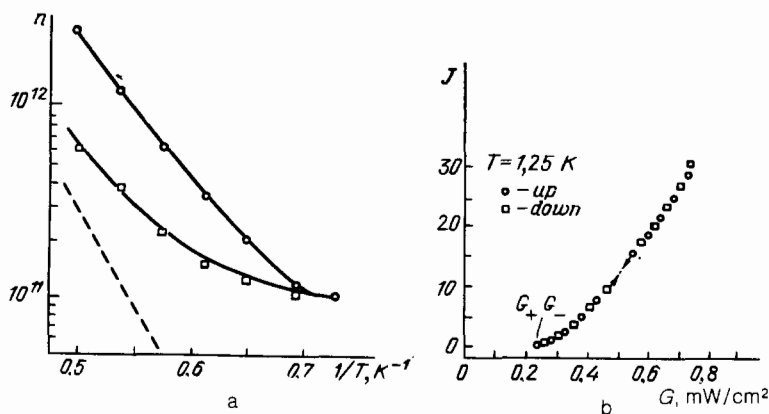


Figure 18 shows the low-temperature part of the phase diagram showing excitons and EH drops<sup>31</sup> and it has been demonstrated that at temperatures  $T \lesssim 1.25$  K the hysteretic behavior of  $J(G)$  disappears, as predicted by the theory.

We shall now consider the case of low temperatures and rapid removal of drops when  $\beta \rightarrow 0$  and  $b \gg a$ ; then, Eq. (20) yields

$$\frac{d\psi}{dv} \approx \ln(1+b) = \ln\left(1 + \frac{1}{\alpha\theta}\right). \quad (23)$$

We thus allow for the removal of drops, but we are still ignoring evaporation and recombination. Substituting Eq. (23) into Eq. (21), we obtain the distribution function

$$g_v = g \exp\left[-\int_1^v \ln(1+b) dv\right]. \quad (24)$$

The physical meaning of Eq. (24) can be determined by considering a sample in the form of a plate of thickness  $d$  with absorbing walls in which drops can move at a transverse velocity  $v$  which generally depends on the number of particles  $v$  in a drop. We shall assume that the rate of attachment of such gas particles to a drop is  $\alpha_v$  and the loss of such particles will be ignored ( $\beta \rightarrow 0$ ). Then, the probability that a drop goes over from  $v$  to  $(v+1)$  and does not reach a wall is

$$W_{v \rightarrow v+1} = \frac{\alpha_v}{\alpha_v + (v_v/d)}.$$

Applying this rule consistently to drops containing one, two, and more particles, we find that

$$W_{1 \rightarrow v} = \prod_i \frac{1}{1 + (v_i/\alpha_i d)},$$

i.e., we obtain Eq. (24).

In other cases when the processes of evaporation, recombination, and removal of drops are equally important, it is not possible to obtain the answer from qualitative considerations and it is necessary to solve Eq. (17).

We shall now analyze the "phase diagram" of the transition. In experiments it is usual to measure the threshold dependence of the concentration of liquid on the degree of supersaturation. Without allowance for the nucleation kinetics a family of such thresholds forms a phase diagram corresponding to  $n = n_s$ , i.e., to the phase equilibrium condition. This  $n(T)$  dependence is represented by the dashed line in Fig. 19. If the system is pure, so that the nucleation kinetics must be allowed for, the dependence  $n(T)$  may correspond to the attainment of some physically reasonable

FIG. 18. a) Low-temperature part of the phase diagram of the transition from excitons to an electron-hole liquid<sup>29</sup>; b) disappearance of hysteresis of  $J(G)$  at low temperatures.<sup>31</sup>

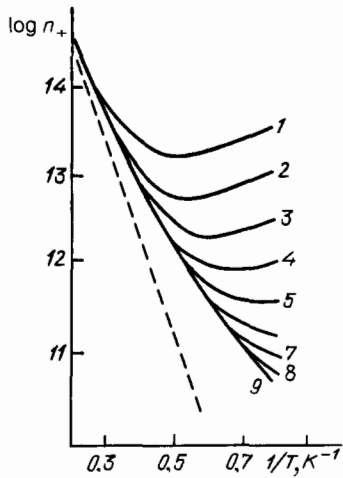


FIG. 19. Phase diagram of the transition from excitons to an electron-hole liquid<sup>45</sup> in crystals of different thickness  $d$  (cm): 1)  $10^{-3}$ ; 2)  $2 \times 10^{-3}$ ; 3)  $4 \times 10^{-3}$ ; 4)  $8 \times 10^{-3}$ ; 5)  $1.6 \times 10^{-2}$ ; 6)  $3.2 \times 10^{-2}$ ; 7)  $4 \times 10^{-2}$ ; 8)  $1.28 \times 10^{-1}$ ; 9)  $2.56 \times 10^{-1}$ .

steady nucleation rate or a given concentration of drops. This is the result of a somewhat arbitrary agreement related to the sensitivity of an experiment; however, since the nucleation rate depends very strongly on the control parameters (degree of supersaturation and temperature), the errors are small. A branch of the phase diagram obtained in this way is essentially kinetic; however, in the case of quasi-equilibrium transitions the kinetic and thermodynamic branches are determined by the free energies of the phases, as well as by the surface tension and temperature. The situation is different in an open system; in this case the threshold degree of supersaturation may be governed either by the finite lifetime of the liquid (which is possible at low temperatures, see Fig. 18) or by the flow of the liquid to absorbing walls.

The kinetic branch of the phase diagram can be constructed by calculating the functions  $\psi_v$  and  $g_v$  with the aid of Eqs. (20) and (21). Such calculations<sup>45-57</sup> demonstrate (Fig. 19) that a reduction in the thickness of a sample should modify strongly the low-temperature part of the phase diagram: instead of the exponentially falling function, we obtain one which rises slightly as a result of cooling. The threshold concentration in a sample of 10- $\mu$ m thickness is close to  $10^{13}$  cm<sup>-3</sup>, which corresponds to a degree of supersaturation  $\approx 10^3$  at  $T \leq 1.5$  K.

Therefore, the low-temperature threshold of liquid nucleation in a thin sample should be independent of temperature and be governed by the ratio between the rate of drop growth and the average velocity of its diffusion toward the surface. At "high" temperatures ( $T \geq 3$  K) the main role is not played by diffusion, but by the competition between the processes of evaporation and attachment of excitons; this branch of the phase diagram is described by Eq. (10).

When the nucleation threshold is governed by the diffusion of tiny droplets, we can confine ourselves to an analysis of the distribution function  $g_v \propto \exp(-\psi_v)$  in the range  $v \leq 10^4$ , because at higher values of  $v$  close to  $v_s$  ( $\approx 10^6$ ) we can ignore diffusion and the shift of the nucleation threshold can only be due to the change in  $g_v$  at low values of  $v$ .

The drift case is somewhat more complex because we have to allow for the drag of drops by external forces<sup>48,49</sup> and their deceleration due to momentum relaxation on a lat-

tice,<sup>50,51</sup> as well as for the capture by immobile centers and detachment from these centers.<sup>52,53</sup> As a result the time  $\theta_v$  governing the flux of drops out of a sample [see Eq. (17)] may be a complex function of  $v$ . Special calculation methods have been developed<sup>46,54</sup> and these made it possible to find not only a smooth fall of  $g_v$  at low values of  $v$ , but also a maximum of this function at  $v \approx v_s$ , and to determine how the amplitude of this maximum varies with the drift conditions.

#### Experimental investigation of nucleation under conditions of diffusion and drift of electron-hole drops

##### 1) Thin samples<sup>45,46,55</sup>

Figure 20 shows the dependence of the intensity  $J$  of the luminescence emitted by a liquid on the rate of pumping  $G$  of three samples of different thickness and with different dopant concentrations. Curves 2 and 2' represent a hysteretic dependence of the appearance and disappearance of a liquid on the rate of pumping of a sample of thickness  $d \approx 1$  mm; curves 1 and 1' are the corresponding dependences for a thin sample ( $d \approx 10$   $\mu$ m). These two samples were prepared from an undoped material ( $N_1 \approx 3 \times 10^{10}$  cm<sup>-3</sup>). Curve 3, which merges with curve 3', shows the dependence  $J(G)$  for a thin doped sample ( $d \approx 10$   $\mu$ m,  $N_1 \approx 10^{15}$  cm<sup>-3</sup>). We can see that the nucleation threshold in a thin sample is higher than the nucleation threshold in a bulk sample, and the difference is almost two orders of magnitude.<sup>5)</sup>

Figure 21 shows the experimentally determined phase diagram of the transition from excitons to an EH liquid in Ge samples of different thickness.<sup>55</sup> We can see that the experimental points fit the theoretical curves well throughout the investigated range of thicknesses; the only fitting parameter was the diffusion coefficient per EH pair.

Therefore, the experimental results are readily explained if we assume that the nucleation of drops is homogeneous, i.e., not related to fixed defects in a crystal. The observation that in the case of a thin doped sample the nucleation threshold is considerably lower than in a pure sample is not in conflict with this hypothesis; in fact, a drop which is nucleated homogeneously may be captured by an impurity center and if the capture time by an impurity is of the order of the time taken by a drop to reach the surface of a sample,

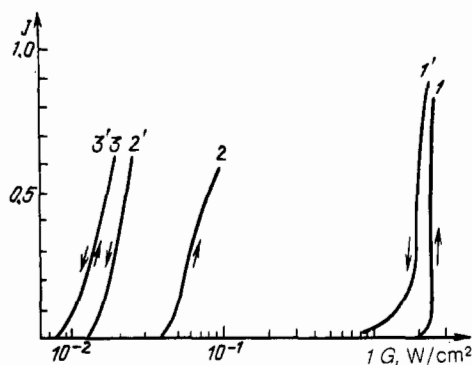


FIG. 20. Threshold behavior of the luminescence emitted by an electron-hole liquid in crystals of different thickness and with different dopant concentrations ( $T = 1.7$  K): 1), 1') metastable and stable branches of  $J(G)$ ,  $d = 19$  cm,  $N_1 = 3 \times 10^{10}$  cm<sup>-3</sup>; 2), 2') metastable and stable branches of  $J(G)$ ,  $d = 0.1$  cm,  $N_1 \approx 3 \times 10^{10}$  cm<sup>-3</sup>; 3), 3')  $d = 10^{-3}$  cm,  $N_1 \approx 10^{15}$  cm<sup>-3</sup>.

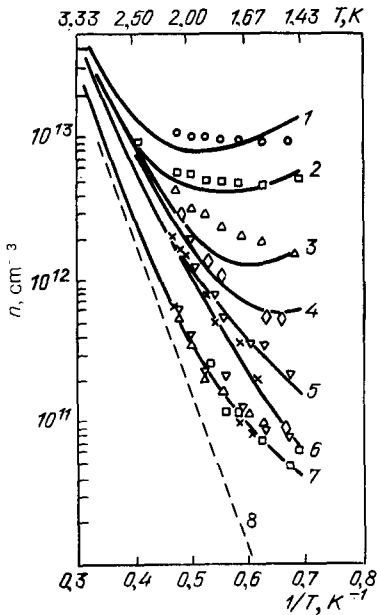


FIG. 21. Phase diagram of the transition from an exciton gas to an electron-hole liquid in samples of different thickness  $d$  (cm): 1) 0.003; 2) 0.005; 3) 0.011; 4) 0.021; 5) 0.085; 6) 0.3; 7) stable boundary of the phase diagram. The continuous lines are calculated on the basis of the theory proposed in Ref. 46. The circles are the experimental values: the open circles show the position of a stable threshold, and the black dots\* represent the position of the metastable threshold. The dashed line is the saturated vapor density.<sup>55</sup>

\*cf. Fig. 2 in Ref. 55 for "black dots".

then the thin sample becomes impermeable for a drop. The heavier the doping of a crystal, the smaller the thickness at which it becomes "thin."<sup>56)</sup>

## 2) Drift motion of drops

Several investigations<sup>40,41,54,56</sup> have been made of a change in the nucleation rate during drift motion of drops. The force acting on the drops was due to a flux of long-wavelength acoustic phonons.

We shall first consider an experiment which could be analyzed approximately using a simple model of drift motion. In this experiment a drop of an EH liquid was excited in a sample not specifically doped with an impurity concentration  $N_i \approx 10^{12} \text{ cm}^{-3}$  and  $d \approx 0.5 \text{ mm}$  thick subjected to a heating microwave field<sup>57</sup> (Fig. 22a). In this figure curves 1 and 1' are the rising and falling branches of  $J(G)$  in the absence of a heating field. We can see that the width of a hysteretic dependence is considerably less than for a pure

sample. We can therefore assume that the nucleation of liquid drops was essentially heterogeneous and due to impurity centers; under the action of an external force (i.e., as a result of microwave heating of electrons) a drop could not move until its size exceeded a certain critical value  $\bar{r}$ . In the range  $r > \bar{r}$  an impurity center could not pin a drop and it left the sample. The nucleation threshold of a liquid in a heating field was shifted slightly, but the slope of  $J(G)$  decreased strongly. Clearly, in a heating field the maximum size of the drops exceeded  $\bar{r}$  (i.e., the size of a drop pinned by an impurity) and the drop left the sample without growing to a stable size  $r_s$ . This reduced the effective lifetime amounting to  $\tau^* \approx 7 \mu\text{s}$  in the case of the curves in Fig. 22a. The motion of drops should suppress hysteresis, which was indeed practically absent in a heating microwave field.

A slight increase in the nucleation threshold (curve 2 in Fig. 22a) was clearly associated with the nonisothermal nature of the nucleation process.<sup>43</sup>

The influence of the drift of the drops in purer samples was more complex. Figure 22b shows the shift of the nucleation threshold under the influence of the phonon wind from a heat pulse generator.<sup>57</sup> An increase in the size of the nuclei increased the nucleation threshold (unfortunately, it also increased the temperature of the sample).

It was found that microwave heating of nonequilibrium electrons and holes<sup>41</sup> was more effective than a heat pulse generator (Fig. 23). In this case it was possible to achieve a large shift of the nucleation threshold without overheating a sample (the width  $G_+ / G_-$  of the hysteresis loop was 20–50 for a constant value of  $G_-$ ).

The increase in the nucleation threshold was explained on the assumption that the nucleation process was homogeneous, but a nucleus moving in a sample could be captured by fixed defects; for example, if a sample of unit volume contained  $N_i$  impurity centers, then the characteristic length  $\lambda$  in which a drop is captured should be  $\lambda = (\pi N_i r^2)^{-1}$ , where  $r$  is the drop radius. The criterion of capture (pinning) is that the thickness of the sample  $d$  should be of the order of  $\lambda$ :

$$\pi N_i r^2 d \approx 1.$$

Therefore, the process of drift was found to be important only in the case of small droplets; large drops were usually captured by defects in a crystal. It is clear from Figs. 21 and 23 that near the nucleation threshold of an EH liquid the intensity of the luminescence emitted by drops changed abruptly. An apparently similar abrupt change in the concentration of the new phase, due to the fact that the only

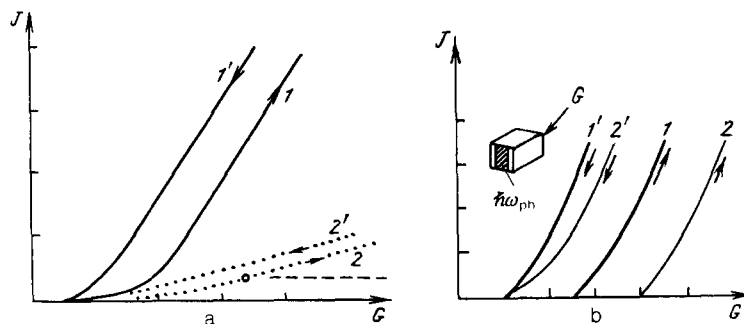


FIG. 22. a) Hysteresis of  $J(G)$  in a heating microwave field at  $T = 1.8 \text{ K}$ : 1), 1') hysteresis in the absence of a microwave field; 2), 2') microwave power  $P \approx 200 \text{ mW}$ . b) Same results but in the presence of a heat pulse<sup>57</sup> ( $T = 1.67 \text{ K}$ ): 1), 1') in the absence of a heat pulse; 2), 2') when the power of a heat pulse is  $0.67 \text{ W/cm}^2$ .

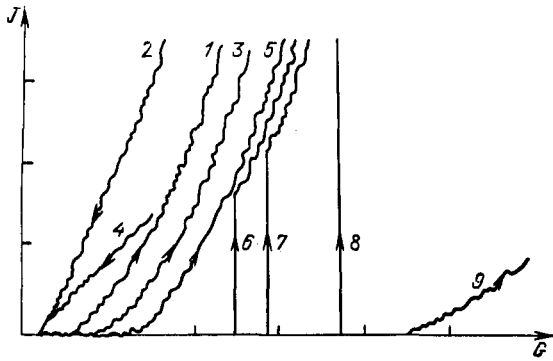


FIG. 23. Abrupt nucleation of an electron-hole liquid in a heating microwave field ( $T = 1.6$  K,  $d = 0.5$  mm): 1), 2) metastable and stable branches of  $J(G)$  in the absence of microwave heating; 3), 5)–9) metastable branch obtained for different relative values of the microwave power  $P = 0.15, 0.2, 0.62, 0.8, 0.92$ , and  $1.23$  for curves 3, 5, 6, 7, 8, and 9, respectively; 4) stable branch for  $P = 1.23$ . The dependence denoted by 8 was obtained for  $P \approx 50$  mW.

“successful” nucleus destroyed the supersaturation of the whole volume, was observed also in the case of quasiequilibrium transitions. However, the abrupt increase in the concentration of an EH liquid was completely unusual. In fact, since the size of a drop of an EH liquid was limited (Fig. 3), an increase in the concentration of the liquid should result in a sequence of microjumps merging into a smooth curve (see, for example, curves 3 and 5 in Fig. 23).

An abrupt change in the concentration of an EH liquid can be explained by assuming that a large number of drops appears practically simultaneously.<sup>40,59,60</sup> A possible explanation of this effect based on the mechanisms of capture of liquid drops by fixed defects in a crystal and detachment from these defects under the influence of external forces is as follows.<sup>54</sup> Drops of an EH liquid nucleated near the illuminated surface of a sample are dragged into the interior by the phonon wind created by electrons that are heated in a microwave field. The drift motion of nuclei has the effect that at pumping rates which may be higher than the nucleation threshold in the absence of a microwave field there is practically no liquid although the concentration of tiny drops may be considerable.

If a nucleus inside a sample collides with an impurity center, it is captured by this center and grows into a macroscopic drop containing  $\nu$  particles ( $\nu_s$  increases on increase in the exciton density).

The force acting on a drop is proportional to the number of particles in a drop; on the other hand, the energy of binding of a drop to a point center is independent of the size of the drop and, consequently, there is such a value of  $\tilde{\nu}$  that for  $\nu > \tilde{\nu}$  the center cannot retain the drop.

If  $\nu_s > \tilde{\nu}$ , a drop pinned by a point center grows, becomes detached, and moves out of a sample without reaching its stable size. If a sample is pure, the average number of drops trapped by point centers is small compared with the total number of drops crossing the sample without reaching macroscopic size. Such a state is metastable; if an external source is used to create a large number of drops at the force centers, the system goes over to a stable state in which all the drops are pinned at point centers, the density of excitons is low, and we have  $\tilde{\nu} > \nu_s$ .

We shall now allow for fluctuations of the rate of nu-

cleation in a metastable state (this may be due to, for example, fluctuations of external pumping). If a large number of drops is formed simultaneously, the exciton density (and, consequently, the value of  $\nu_s$ ) falls and it may turn out that  $\nu_s < \tilde{\nu}$ . In this case all the nucleated drops remain in the sample, i.e., the system “remembers” a single sufficiently large fluctuation. Therefore, for the same average pumping rate we can have two different states of a system: “static” when drops are at rest and there is practically no nucleation and “flow” when the nucleation rate is high and the bulk of the drops leave the sample without reaching macroscopic size, while a small proportion of drops is captured by centers, grows to  $\nu > \tilde{\nu}$ , becomes detached, and leaves the sample.

The transition from the “flow” to the “static” state due to competition between the pinning and detachment effects occurs in a time which is short compared with the lifetime of the liquid and which decreases on increase in the degree of supersaturation.<sup>60</sup>

We shall conclude this section with a few words about a critical nucleus in an open system, i.e., about a drop which reaches macroscopic size with a near-unity probability. The concept of a critical nucleus has been fruitful in the case of quasiequilibrium transitions when the critical size has a clear physical meaning and corresponds to the maximum of the difference between the thermodynamic potentials  $\Delta\Phi$  (Fig. 1). In open systems from which drops can escape by diffusion or drift the size of a drop corresponding to the equality of the rates of pinning and evaporation of gaseous particles is not related, as shown in Ref. 46, to the characteristic features of the function  $\Delta\psi$  or the function representing the size distribution of the drops [see Eq. (24)]. Therefore, a nucleus critical in the usual sense of the word does not play the same role in the case of open systems. Nevertheless, we can introduce a concept of a critical nucleus of such a drop which is practically immobile because of a large mass (in the case of diffusion) or which is trapped by an impurity (in the case of drift). However, since there are several methods of making a system open, the definition of a critical size then ceases to be universal.

## CONCLUSIONS

Recent investigations discussed in the present review have resulted in a better understanding of the kinetics of a first-order phase transition and in further progress in the macroscopic concept of nucleation. An important circumstance confirming the correctness of our ideas on the kinetics of nucleation is the experimental proof of the existence of two nucleation regimes: steady-state and transient, which are characterized by two different time constants. The step which is next in importance is the development of these ideas for the case of open systems which are far from equilibrium and for which the description of a phase transition is based on kinetic and not thermodynamic characteristics of the system. Probably the most surprising result is that even at a very high degree of supersaturation when one might expect manifestation of the nonideal nature of the initial phase, the process can be described satisfactorily by macroscopic average frequencies of trapping (capture), evaporation, and recombination. The finite lifetime of a liquid can be allowed for by supplementing a simple model of diffusion across a barrier (Fig. 1) with the concept of a steady-state size  $r_s$  (Fig. 17).

If drops can still leave the volume of a sample in a time  $\theta$ , we have to allow for the motion of a particle with a finite lifetime  $\theta$  in the space of its dimensions. In most cases of practical importance a critical nucleus consists of a large number of particles and it can be considered macroscopically.

An important experimental result is that the threshold of nucleation of a new phase can be varied by a factor of many hundreds and thus approach the limit of absolute stability (i.e., the spinodal<sup>61,62</sup>). Similar kinetic effects should probably be exhibited by other physical systems described, for example, in the review of Merzhanov and Rumanov.<sup>63</sup> In particular, a shift of the nucleation threshold of an EH liquid in a thin germanium sample is clearly analogous to an increase in the threshold of a chain reaction of combustion of a gas in a tube with cold walls (this was the effect used in the miner's lamp proposed by Davy).

L. N. Cooper<sup>64</sup> said that "aiming and then shooting produces a different result than shooting followed by aiming." Following this principle, we tried at least not to distort other aspects of the problem of nucleation which are not dealt with in the present paper.

However, even in the specific topic of steady-state and transient nucleation we are far from full understanding. The theory of this process is still essentially qualitative: the solution of Eq. (4) for realistic initial and boundary conditions has not yet been obtained, with the exception of the quasi-steady regime.<sup>35</sup> The problem is not simply mathematics: we do not know how to formulate the problem in the case of drops consisting of a small number of particles. This problem is ignored in the modern kinetic theory and this is justified if the binding energy of tiny drops is negative at all values of  $v$ , i.e., if drops of all dimensions are stable. It has been shown that this is indeed true, for example in the condensation of argon.<sup>65</sup> Exciton molecules have been observed<sup>66</sup> in the transition from excitons to an EH liquid in Ge and Si. However, more complex entities ("trions", etc.) have not been observed; therefore, the problem of the smallest drops is still to be solved. If such drops (complexes) are unstable, a nucleus should form as a result of a random simultaneous encounter of a large number of particles (which is extremely unlikely and in any case does not agree with the experimental results).

In general, it is necessary to refine the concepts of homogeneous and heterogeneous nucleation; we have already mentioned that the nucleation of an EH liquid in pure Ge samples is on the one hand homogeneous (small drops in a thin sample are free) and, on the other, the nucleation threshold depends on the impurity concentration. A possible resolution of this conflict would be to assume that a drop can be nucleated at an impurity, but if the binding energy of a tiny droplet is small, it becomes easily detached from the impurity as a result of thermal fluctuations and then moves freely in the crystal.

The author is deeply grateful to Ya. B. Zel'dovich, whose corrections and suggestions played a key role in the writing of this paper, and to V. M. Asnin and B. M. Shklovskii, who read the manuscript and made valuable comments.

<sup>11</sup>It should be pointed out that under conditions such that a gas is unsaturated and a liquid is not formed, drops can form as a result of fluctu-

ations and then can evaporate rapidly. A qualitative concept of such "precondensation" and "premelting" fluctuations was put forward by Frenkel<sup>1</sup>; later, Andreev<sup>7</sup> showed that these fluctuations give rise to singularities of thermodynamic quantities near the phase separation point.

<sup>21</sup>It follows that the saturated vapor density depends on the curvature of a drop; in the general case of a nonspherical nucleus this density is governed by the average (not by the Gaussian) curvature.

<sup>31</sup>We recall that we are speaking of "diffusion" along the  $r$ -size axis and not of diffusion of a gas in ordinary space.

<sup>41</sup>The influence of the drift of nuclei out of a sample is discussed in Sec. 3; the nonisothermal nature of nucleation is the effect of overheating of a nucleus by nonequilibrium electrons and holes which are incident on it. This effect is usually small<sup>42</sup> and its major role in the case of a transition from excitons to an EH drop is due to the finite lifetime of excitons, i.e., it is due to the initial nonequilibrium of the gaseous phase.<sup>43,44</sup>

<sup>51</sup>The thickness of a plate is less than the diffusion length of excitons and the surface recombination velocity is high so that the density of excitons is proportional to the rate of excitation and is independent of the thickness of a sample.

<sup>61</sup>However, we cannot say that the problem of homogeneous and heterogeneous nucleation is now fully understood. In fact, the nucleation threshold in a doped sample is not simply low, but it is lower than even in a pure sample (there is no hysteresis in the case of curves 3 and 3' in Fig. 20); therefore, impurities play a certain role in nucleation and we can speak only of the "effective" homogeneity, i.e., that drops of sufficiently large size are mobile.

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Translated by A. Tybulewicz