On the theory of fog

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It is pointed out that in first-order phase transitions nucleation stops when the supersaturation decreases by a small amount. A simple quantitative description of the next stage of the kinetics of the transition — the growth stage — is proposed. This stage lasts much longer than the nucleation stage, and during practically the entire duration of this stage all nuclei have virtually the same size and the number of nuclei is constant, and the main drop in supersaturation occurs here. © *1996 American Institute of Physics.* [S0021-3640(96)01313-8]

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Two stages are distinguished in the kinetics of first-order phase transitions — nucleation and coalescence (see, for example, Ref. 1), corresponding to the initial and final (in time) asymptotic solutions of the nonlinear equations governing the size distribution function of the nuclei of the new phase. The general solution cannot be obtained, but a quite complicated analysis of the equations led Maksimov and Mikhaĭlov[2] to the conclusion that there exists a special intermediate stage — the growth stage. The main distinction of this stage is that the number of nuclei is almost constant. It is conjectured that the growth stage, which "joins" the limiting solutions, develops at times when the supersaturation has fallen off by an amount of the order of the initial supersaturation. In the present Letter, it is pointed out that this is not so — the probability of the appearance of new nuclei must be neglected much earlier, when the degree of supersaturation has decreased only by a small amount. This substantially simplifies the problem: It is found that practically all nuclei possess the same size during virtually the entire growth stage.

The rate of nucleation s is determined mainly by the exponential $\exp(-U/T)$ (in the present work, we shall employ the notation and concepts introduced in Ref. 1). Since it makes sense to discuss only the limit of small supersaturations, when $U(a_c) \gg T$, as the supersaturation decreases and the critical size a_c of the nuclei correspondingly increases, the process producing new nuclei switches off exponentially when the change δU in the formation energy of critical nuclei exceeds the temperature, i.e. (see Ref. 1),

$$\delta U = 2U\frac{\delta a_c}{a_c} = -2U\frac{\delta\Delta}{\Delta} \sim T. \tag{1}$$

As we shall see below, the change $\delta\Delta$ in the supersaturation is quite small. Its time dependence follows from the law of conservation of the particle number: $\delta\Delta(t) = -q(t)$, where $q(t)$ is the number of particles which have precipitated out of the

solution into the nuclei as determined by the well-known size distribution function $f(a)$ of the nuclei at the nucleation stage (see Eq. (99.8) in Ref. 1):

$$f=sf_0\int_a^\infty \frac{da}{Bf_0}. \tag{2}$$

At this moment in time, most of the particles that have precipitated out of the solution are located in nuclei whose radii are large compared with the critical radius. The integral (2) for $a\gg a_c$ can be easily calculated, using the fact that it converges exponentially for large sizes. Expanding the integrand near the lower limit, we obtain

$$f\approx \frac{s}{B}\int_0^\infty \exp\left(-\frac{8\pi\alpha a}{T}x\right)dx=\frac{s}{Dv'\Delta}a. \tag{3}$$

The linear behavior of the distribution function (3) is correct for sizes much greater than the critical size, but, evidently, smaller than the maximum radius a_m of the nuclei which arose first after the supersaturation was "switched on." For our purposes, it is sufficient to assume that the distribution function is given by expression (3) right up to $a=a_m$ and equals zero for large sizes. The rate of growth of the transcritical nucleus equals

$$\dot{a}=\frac{2\alpha Dv'^2c_{0\infty}}{Ta}\left(\frac{1}{a_c}-\frac{1}{a}\right) \tag{4}$$

(see the problem in Sec. 99 of Ref. 1). If nucleation stage lasts for a time t_0, then for $a\gg a_c$ we find from Eq. (4)

$$a_m^2=2Dv'\Delta t_0. \tag{5}$$

The total number of particles which have precipitated out of the solution into the nuclei equals

$$q(t_0)=\frac{4\pi}{3v'}\int_0^{a_m} fa^3da\approx\frac{4\pi}{15}\frac{s}{Dv'\Delta}a_m^5. \tag{6}$$

Therefore, substituting expression (6) into condition (1) and taking account of Eq. (5), we find the time t_0

$$t_0\sim \exp(2U/5T), \tag{7}$$

after which nucleation should be neglected, but there are still no reason for coalescence to occur, and the transcritical nuclei will continue to grow with their number N remaining constant:

$$N=st_0\sim \exp(-3U/5T). \tag{8}$$

We note here that if the nucleation stage (i.e., thermally activated "passage" of the nuclei through the critical radius) does not occur at all in the system on account of the appearance of nuclei at impurities, the kinetics of the transition starts immediately with the growth stage. Then N equals the number of impurities — the effective condensation centers.

The average size of the transcritical nuclei at the stage being considered is $\langle a\rangle\gg a_c$. At the start of the growth stage, the decrease in the supersaturation can still be

neglected when determining the growth rate of the nuclei. Then, from Eq. (4) we obtain for the time dependence of the radius of nuclei which are appreciably larger than the critical size

$$a^2(t)=2Dv't+a^2(0), \tag{9}$$

and therefore after a time which is short compared with the duration of the entire growth stage but longer than the duration of the nucleation stage, the average size of the nuclei will greatly exceed the characteristic width of the distribution function

$$\delta a=a_m^2/\langle a\rangle. \tag{10}$$

Therefore the description of the further growth after this initial growth stage simplifies substantially, since it can be assumed that all nuclei have the same size $\langle a\rangle$. The total number of particles in the nuclei in this case equals

$$q=\frac{4\pi\langle a\rangle^3}{3v'}N, \tag{11}$$

and the growth of the nuclei is determined by the equation

$$\tau\dot{x}=\frac{1}{x}\left(1-x^3-\frac{\epsilon}{x}\right), \tag{12}$$

where

$$x=\frac{\langle a\rangle}{b},\quad \tau=\frac{b^2}{Dv'c_{0\infty}}\sim\left(\frac{U}{T}\right)^{2/3}t_0,\quad \epsilon=\frac{a_{c0}}{b},\quad b=\left(\frac{3v'\Delta}{4\pi N}\right)^{1/3}. \tag{12a}$$

The approximation of the distribution function by a δ-function will become inapplicable when at a time $t_1\gg t_0$, as the nuclei grow, the supersaturation decreases to where the critical size reaches $\langle a\rangle$. The supersaturation then equals

$$\Delta(t_1)=\frac{2\alpha v'c_{0\infty}}{a_c(t_0)}\approx 2\alpha v'c_{0\infty}\left(\frac{4\pi N}{3v'}\right)^{1/3}\sim\exp\left(-\frac{U}{5T}\right). \tag{13}$$

Up to this time the growth of the nuclei is governed by the expression

$$\frac{t}{\tau}=\frac{1}{3}\ln\frac{\sqrt{x^2+x+1}}{1-x}+\frac{1}{\sqrt{3}}\tan^{-1}\frac{\sqrt{3}}{2x+1}. \tag{14}$$

Here the last term $\sim\epsilon$ in Eq. (12) was dropped in the calculation. This term could become important as the critical radius approaches the average radius, but the breakdown of the δ-function approximation of the distribution function turns out to be more important. From Eq. (14), taking account of the cutoff of the logarithmic divergence as $1-x\to 0$ at a value equal to the relative width of the distribution function $\delta a/\langle a\rangle\sim(a_m/\langle a\rangle)^2$, we find

$$t_1=\frac{2\tau}{3}\ln\frac{b}{a_m}\sim t_0\left(\frac{U}{T}\right)^{2/3}\ln\left(\frac{U}{T}\right). \tag{15}$$

At the moment t_1 when the "δ-function" no longer works (i.e., when the rate of change of the average size $\langle a\rangle$ equals zero) $\langle a\rangle=a_c$. We note that the state in which all

nuclei have the same radius — equal to the critical radius — is an exact (but unstable) solution of the kinetic equations [Eqs. (100.4) in Ref. 1]. Since, however, the distribution function has a finite width, the nuclei which are larger than the critical size continue to grow and smaller nuclei start to dissolve, i.e., the final stage of the phase transition — coalescence — starts. The distribution function will start to broaden. The number of nuclei, however, will not change for a long time yet (since on account of the strongly decreased supersaturation, the kinetics slows down substantially), and it will start to decrease only when the dissolved nuclei traverse the distance from $a_c(t_1)$ to zero. After the time t_1 (with the exception, evidently, of the start of the process of broadening of the distribution function) and before the long-time asymptotic is reached, the problem can apparently be solved only by numerical methods.

We note that in Ref. 1 a more complete investigation of the growth stage was actually performed: The size distribution function of the nuclei was found at times which include the nucleation stage, the transition from the nucleation stage to the growth stage, and the growth stage itself. However, the quantity C in the formulas (4.10) and (4.11) in Ref. 2 is not a constant of the order of 1, but rather it is an exponential function of the large parameter x_0, and the characteristic times t_0 and t_1 introduced above also appear. It is also easy to see that the distribution function presented in the footnote on page 1375 of Ref. 2 reduces to a δ-function at times $t_0 \ll t \ll t_1$.

We note that since the stage being discussed is largely determined by the growth kinetics of nuclei which are much larger than the critical nuclei, the quantitatively obtained relations hold only for the condensation of a liquid from a gas (liquid) solution, where there are no reasons for dendritic instability (the hydrodynamics inside a nucleus will guarantee minimum surface energy (spherical nuclei)). As small crystals precipitate from a solid solution, the nuclei which are much larger than the critical sizes are unstable and the growth law of dendrites under the conditions of decreasing supersaturation, considered above, has yet to be determined. However, we see no reason why the qualitative picture (small variance of the size distribution function of the nuclei) should change.

It is very likely that the picture proposed here describes ordinary fog, which arises when water condenses from air. In this connection, it would be interesting to measure the size distribution of droplets in fog (as well as rain droplets and small snowflakes).

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