Particle Log-Size Standard Deviation as a Numerical Criterion to Distinguish Some Mechanisms for Nucleation and Growth

Vitali V. Gavrik, Cologne, Germany

Annotation

The formation mechanisms for particle size distribution are of high interest in the theory and practice of emulsion preparation. A stable log-size standard deviation, LS, keeps often their ripening stage. The least LS of „monodisperse" emulsions is produced by double-jet precipitation (0.08 to 0.12 in log-radius scale). Granqvist and Buhrman noted the LS of ultradisperse particles to tend to several values correlated to some preparation techniques that they assumed to provide free coagulation and to result in log normal distribution. A mathematical procedure elaborated to study the processes has detected a mistake in the suggestions. The mechanism leads actually to the Smoluchowski distribution of volumes, or the Weibull distribution of radii with the unique LS value. Emulsion microcrystals have never been observed to tend to the stable LS, thus indicating no emulsion precipitation process to be the free coagulation. Another process with the smallest particles only adding to one another or to their aggregates has been shown to explain one more stable LS value and to fit the latent image formation as well as precipitation of monodisperse emulsions.

Introduction–Size Distributions of Ultradisperse Solids. Inadequacy of LogNormal

Formation mechanisms of silver halide microcrystals are of high importance in modern photographic engineering. Monodisperse emulsions, T-crystals, two- or multilayered crystals underlie the recent progress in high-speed and high-resolution color photographic materials. The lack in quantitative theoretical mechanisms for the monodisperse precipitation is restraining new developments. A look at the problem as a part of the general theory of ultradisperse solid particles may be a valuable assistance. It is intensively developing to meet the needs of thin solid films in microelectronics, applied surface catalysts, composite metal-polymer materials, ultradisperse metal powders, and environment aerosols[2].

The ultradisperse phases often tend to several stable values of particle size variation coefficient, VC, or log-size standard deviation, LS, correlated to some definite preparation techniques under a wide variety of experimental conditions as to Granqvist and Buhrman[2]. All the techniques were assumed by them as providing every particle to add randomly to another and thus resulting in a log-normal distribution, LND, with different stable LS values.

The LS stability was noticed long ago in the course of photographic emulsion ripening. The LS of different emulsions also appeared to gather around some stable values. The smallest one, being 0.08 to 0.12 in log-diameter scale, is characteristic to the monodisperse emulsions formed by the double-jet precipitation. Size distributions were positively skewed and assumed in both the cases to tend to the LND[1,2], as it was done with no sufficient reasons for other such distributions[3]. Their cumulative frequency curves did not turn into straight lines on the probability-logarithmic scale (PL) and consisted of several regular components[1]. "Application of the log-normal formula to the size-frequency distribution of the grains of more common photographic emulsions and of precipitates in general is usually complicated by the presence of "breaks" in the distribution... Frequently, the graphical size distribution assumes a form composed of segments with relatively sharp breaks between them, so that no enclosed formula applies accurately[1]."

All the known mechanisms for the LND formation[5] did not lead to a stable LS. Nevertheless, Granqvist and Buhrman[4] used one based on the central limit theorem of the theory of probability when it was applied to the logarithm of relative increase in particle volume[3-5]. Its necessary condition to hold is the statistical independence of particle log-volume increment, Δlnv, upon the log-volume, lnv, of the particle at any process stage. The statistical distribution of Δlnv (in particular its mean) should not vary with lnv.

Unfortunately, the condition does not hold for the free coagulation assumed. The smallest particle at a process stage receives a volume increment larger than $ln2$ since it can add a random particle only that is certainly larger than itself. Its probable increment significantly exceeds $ln2$. The largest particle can receive a random increment only smaller than $ln2$. The dependence of random increments on particle size makes the application of the central limit theorem improper. Moreover, the mechanism should produce the LS that continuously increase. The process rather produces particle statistics that simulate the LND and keep a stable LS as a result of inherent mathematical properties of distribution function.

A Mathematical Procedure to Study the Statistics of Phase Condensation Processes

A mathematical procedure was elaborated to study the particle statistics in the condensation course of a new ultradisperse phase.

The processes break commonly into nucleation and growth stages. The latter influences predominantly the mean particle size. It is often a linear process controlled by the supply of chemicals and keeping the initial character of distribution function formed at the nucleation stage.

The nucleation seems to be responsible for the statistical moments of higher order. It is assumed below to occur in a restricted volume containing a number of initial particles. It proceeds until all the particles are exhausted or their concentration becomes so small that their collisions with other particles are unlikely. The collision probability in a disperse phase depends upon the random neighborhood and can be assumed not to depend on the particle size[8,9].

A condensation process can be reduced to a simple sequence of independent elementary two-particle collisions. Inefficient collisions that do not result in a particle combination have no effect on the ultimate size distribution. A simultaneous collision of three or more particles is equivalent in statistical sense to a corresponding number of two-particle collisions. At every elementary step, we replace:

- a next collision of two random particles by the mathematical expectation of all the possible two-particle collisions;
- the variation in number of particles of a definite size by the expected variation in their probability to occur in the system after the collision.

The approach enables to evaluate variations in the size statistical moments with the number of collisions. The size distribution function can be sometimes also determined as well as, in some cases, a kinetics solution. An example is the free coagulation below.

A stable LS corresponds to a stable size variation coefficient, η, being nearly identical especially in the region of their small values: $\sigma_{ln} \approx \eta$. An accurate relation depends on the distribution function and, for positively skewed distributions, could be successfully approximated with that of LND:

$$\sigma_{ln} = ln\ \sigma_g = [ln\ (1+\eta^2)]^{0.5}, \quad (1)$$

σ_g is the geometric standard deviation, GS, sometimes used[2].

Free Coagulation. Smoluchowski/Weibull Particle Size Distribution

The inadequacy of LND under the free coagulation conditions led to approximations of size distribution with the Gauss function[6], or a combination of the distributions[7]. The mechanism was shown long ago to result in the Smoluchowski distribution of particle volumes[8,9] or to the Weibull distribution of their diameters or projective areas[10,11].

In LND approximation[2,12], the particle size distributions formed under the conditions of free coagulation possess the GS of 1.48 ± 0.12 and their mean LS is about 0.35. The ultradisperse powders were obtained by metal evaporation or explosion of metal wire in noble gas atmosphere by a current impulse[13-15]. In the processes, even large particles are mobile and can add to each other. Their spatial disposition is random and interparticle distances are large enough for the collision probability not to be considerably influenced by the particle size. Some complex kinetics calculations and experiments showed ultradisperse aerosols by the Brownian coagulation[16] to possess $\sigma_{ln} \approx$ 0.34-0.4. The CV „in the uniform portions" of rainclouds[17] also tends to about 0.36.

Let N particles of mean size, $M_o = a$, aggregate when collide. Consider several sequential collisions and calculate the portions of different aggregates, with accounting for all the random states of the system after a next collision. After a first collision, the system contains N -2 particles of initial size, $n = 1$, and an aggregate of $n = 2$ particles. Their relative portions in the system are:

$$p_{1,1} = (N - 2)/(N - 1) \text{ and } p_{2,1} = 1/(N - 1). \quad (2)$$

At the next collision, an initial particle can add to one in (N -3) such particles or with the single 2-aggregate. The total number of collision variants is (N -1)(N -2). If the process was multiply repeated at the state, the mathematical expectation of the portion of initial particles remained would be:

$$p_{1,2} = (N - 2) - 2(N - 3)/(N - 1) - 2/(N - 1) = \\ = (N - 2)(N - 3)/(N - 1). \quad (3a)$$

The mean portion of 2- and 3-particle aggregates:

$$p_{2,2} = 1 + (N-3)/(N-1) - 2/(N - 2) = 2(N - 3)/(N-1), \quad (3b)$$
$$p_{3,2} = 2/(N - 1). \quad (3c)$$

The probabilities of the initial particle, 2- or 3-particles aggregate to occur in the system after two collisions are:

$$P_{1,2} = (N - 3)/(N - 1),\ P_{2,2} = 2(N - 3)/(N - 1)(N-2), \quad (4a)$$
$$P_{3,2} = 2/(N - 1)(N - 2). \quad (4b)$$

After three collisions, the probabilities of initial particle, 2-, 3- or 4-particles aggregate to occur are:

$$P_{1,3} = (N - 4)/(N - 1),\ P_{2,3} = 2(N - 4)/(N - 1)(N-2), \quad (5a)$$
$$P_{3,3} = 6(N - 4)/(N - 1)(N - 2)(N - 3), \quad (5b)$$
$$P_{4,3} = 6/(N - 1)(N - 2)(N - 3). \quad (5c)$$

After k collisions, the probability to find the aggregates of n particles is at $0 \le k \le N$ -2 and $1 \le n \le k$ +1:

$$P_{n,k} = (N - k - 1)\cdot\Gamma(k + 1)\cdot\Gamma(N - n)/\Gamma(N)\cdot\Gamma(k - n + 2) = \\ = (N - k - 1)k(k - 1)...(k - n + 2)/(N - 1)(N - 2)...(N - n), \quad (6)$$

Γ is the gamma-function. Sedimentation or freezing[13-15] or the dramatic decrease in concentration can drastically lower

the collision probability and stop coagulation at a late stage. The collision number, k, is very large at even small k/N as N is many orders magnitude. As the aggregates of $n << k$ particles only have a considerable probability to occur and the mean aggregate size is:

$$m = M_k / M_o = N/(N - k) >> 1, \quad (7)$$

an exponential distribution of volume, $v = na$, appears:

$$p_{n,k} \cong (N/k)^{-n} (N - k)/k \cong m^{-1} \exp[-n/m]. \quad (8)$$

The initial particle size distribution or process rate variations in time have no effect on the distribution if only the random sticking condition is met. Substituting $\alpha t = k/(N - k)$ turns Eq. (8) into that of coagulation kinetics derived by Smoluchowski[8,9]:

$$p_{n,t} = [\alpha t/(1+ \alpha t)]^n / \alpha t, \quad (9)$$

α is a rate constant and t is the process time. The kinetics restriction impressed sometimes an exaggerated importance of collision rate in forming the distribution[20].

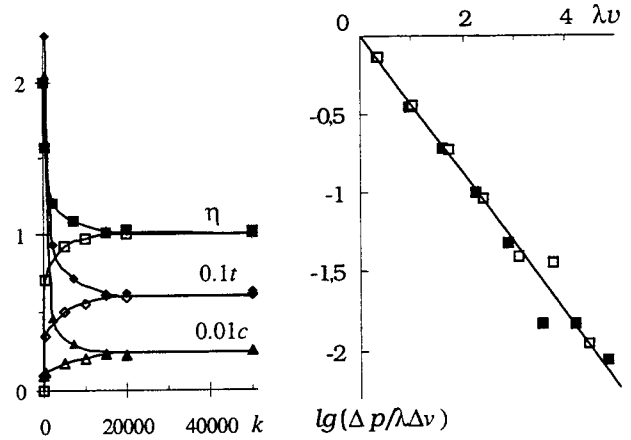

Figure 1. a) Computer simulation of normalized distribution moments in a sequence of k random two-particle collisions: the VC, third and fourth moments. b) Particle volume distribution density after the free coagulation. Initial particle size distribution: LND, η_o = 2.0 (filled figures), monodisperse, η_o = 0 (empty figures).

At a histogram interval d $v >> a$, Eq.(8) turns into:

$$dp(v) = \lambda \exp[-\lambda v]\, dv, \quad (10)$$

$1/\lambda = am$ is the mean particle volume and standard deviation. The LS is $\pi / 6^{0.5} = 1.28$, and the VC:

$$\eta^2_k = D_k [n]/M_k^2 = (N - k - 1)k /(N - k + 1)N \cong k/N \to 1. \quad (11)$$

If the initial particles are polydisperse ($\eta_o > 0$), a rapidly decreasing term, $\eta_o^2 (N - k)/N \to 0$, adds to Eq.(11). The VC of n-aggregate size as a sum of independent random variables should be proportional to $1/n^{0.5}$ and tend quickly to 0, as the relative aggregate differences got negligible. Thus, the ultimate size distribution coincides with that formed by initially monodisperse ($\eta_o = 0$) particles of identical mean size, a.

Computer simulation (Fig. 1a) showed the initial l-order moments (l = 2, 3 and 4) divided by the mean to the power l to tend to 2, 6 and 24. These are the moments of distribution (10) that are equal to $\Gamma(1+ l) = l!$ A LND with the same $\eta = 1$ would give[5] 2, $(1+ \eta^2)^3 = 8$ and $(1+ \eta^2)^6 = 64$. An initial LND with $\eta_o = 2$ was simulated by a generator of normally distributed numbers than exponentiated. The colliding particles were chosen by the standard generator of random numbers. Final number of particles, $N - k$, was 500. Both the histograms (Fig.1b, k/N = 0.99) coincide with one another.

They deal usually in the practice with particle radii, $r = cv^{1/3}$, that obey[10] a Weibull distribution[18] (Fig. 2b) with $\lambda^* = \lambda/c^3$:

$$dp(r) = 3\lambda^* r^2 \exp[-\lambda^* r^3] dr. \quad (10a)$$

In contrast to the monotonic exponenta (10), its asymmetric graph is hardly distinguished from that of LND. Its normalized initial moments are equal to $\lambda^{*-l/3} \Gamma(1+ l/3)$ and the radius VC is 0.364. Its third and fourth moments are only 3 and 11% less than those of LND at the same VC.

The cumulative frequency function is then:

$$P(r) = 1 - (k/N)^n = 1 - \exp[-\lambda^* r^3]. \quad (12)$$

On the PL scale that turns a cumulative LND graph into a straight line, Eq.(12) shows some deviations in the region of small particles (Fig. 2b). Similar deviations were commonly observed in the experiments[2,13]. An arbitrary GS value obtained from the main "straight" portion is 1.48. The preparation techniques of electron microscopic samples that make even large silver particles move and coagulate[19] give their radius VC close to the theoretical 0.36 of Weibull distribution. Its actual theoretical GS is $\exp[\pi/54^{0.5}] \approx 1.53$ and its LS is always 0.43.

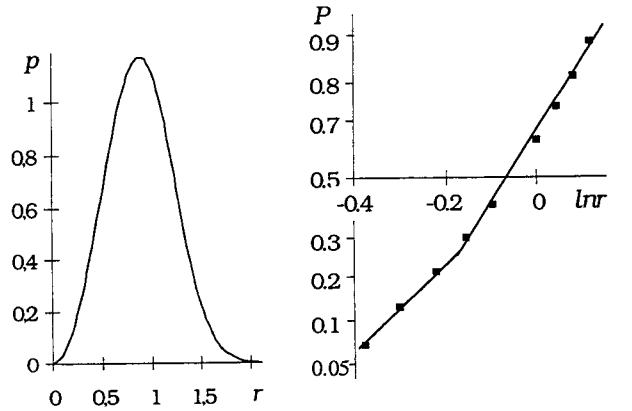

Figure 2. a) Weibull distribution density of particle radii, $\lambda^* = 1$; b) the distribution function on the probability-logarithmic scale.

Thus, the free coagulation leads to the radius distribution that is hardly distinguished graphically from a LND. Its LS of 0.43 is proved for numerous data on the particles coagulated in those processes. Silver halide

emulsion microcrystals display no evident preference of the value. Their LS vary in a wide range from 0.1 to 0.6 and suggest no emulsion preparation techniques to use the free coagulation.

Particle Aggregates Capable to Combine with Initial Particles Only

The smallest particles that only are capable to add (e.g., only mobile) randomly to each other or to their (e.g., immobile) aggregates have been shown recently[21] to explain the constant LS about 0.3 and to fit the latent image formation. The corresponding GS of 1.32 ± 0.12 were observed, for instance, by evaporating silver or gold[22,23] onto solid surfaces, and by chemical application of the ultradisperse particles of metal catalysts onto solid surfaces[24-27]. The close values, 1.34 ± 0.13, were recorded in highly stabilized gold sols[28] with efficient prevention of large particles to combine with one another. The cumulative frequency curves looked the straight lines on the PL scale[2].

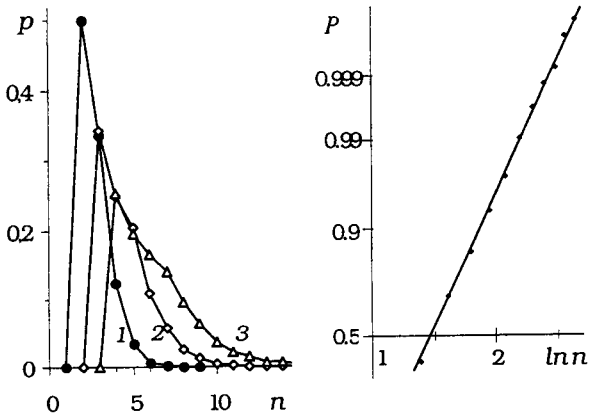

Figure 3. a) Particle size distribution formed by mobile: 1 - initial particles only (e.g., atoms); 2 - to two-particle aggregates; 3 - to 3-particle aggregates. b) The cumulative frequency curve (n_m = 2) on the probability-logarithmic scale.

In the cases, the nucleation and growth occur mainly through a direct random supply of atoms and little-atomic clusters from vapor[29] or solution as well as trough decomposing complex molecules of a chemical surface phase. Mobile 2-, 3- and 4-atom clusters were observed on the solid surfaces[30]. Larger metal islands migrated and coalesced in thin solid films[31], increasing the LS[32] already at 50^0.

Let B, T, and C to be the second, third and fourth initial statistical moments of N mobile particles. In a monodisperse system, $M_o = a$, $B_o = a^2$, $T_o = a^3$, and $C_o = a^4$. In a polydisperse system, normalized $b_o = B_o/M_o^2$, $t_o = T_o/M_o^3$, and $c_o = C_o/M_o^4$ are not equal to 1. Sequential k elementary acts of adding a mobile particle to another randomly chosen lead to:

$$M_k = Na/(N - k), \qquad (13)$$
$$b_1 = B_1/M_1^2 = (b_o+2/N)(N-1)/N,$$
$$b_2 = \{b_o+2[1/(N-1)+1/(N-2)](N-1)/N\}(N-2)/N,$$
$$b_3 = \{b_o+2[1/(N-1)+...+1/(N-3)](N-1)/N\}(N-3)/N...$$
$$b_k = \{b_o+2[1/(N-1)+...+1/(N-k)](N-1)/N\}(N-k)/N \equiv$$
$$\equiv (N-k)\{b_o+2\ln[N/(N-k)]\}/N \qquad (14)$$

as, at large N, the sum in square brackets from i = 0 to k - 1 of $1/(N - k + i)$ coincides with the integral from 0 to k - 1 of $1/(N - k + x)$ with respect to x.

A maximum collision number, K, is limited by the exhaustion of mobile particles. After the first efficient collision, $N_{m,1} = N - 2$ mobile particles remain. The probability of one of them to add to another mobile particle is $p_{m,2} = (N-3)/(N-2) = 1-1/(N-2)$, and its probability to add to the single immobile particle is $p_{i,2} = 1/(N-2)$.

That results in mathematical expectation of mobile particles remained after the second collision, $N_{m,2} = N_{m,1} - 2p_{m,2} - - p_{i,2} = (N-3)[1-1/(N-2)]$, and in that of immobile particles, $N_{i,2} = N_{i,1} + p_{m,2} = 1+ (N-3)/(N-2)$. At the third sticking, the probability of a new immobile particle to appear is $p_{m,3} = 1- -1/(N-2) -1/(N-3)$ and the probability of an immobile particle to grow is $p_{i,2} = 1/(N-2)+1/(N-3)$. The expectation of mobile particles is $N_{m,3} = N_{m,2} - 2p_{m,3} - p_{i,3} = (N-4)[1-1/(N - - 3) - 1/(N-2)]$, and that of immobile particles is $N_{i,3} = N_{i,3} + p_{m,3} = 1+(N-4)/(N-3)+(N-4)/(N-2)$. Then after k collisions:

$$N_{m,k} = (N-k-1)[1-1/(N-k) -1/(N-k+1)...-1/(N-2)]. \qquad (15)$$

When the last mobile particle vanishes:

$$1 - 1/(N-K) +1/(N-K+1)...+1/(N-2) = 0, \qquad (16)$$
$$\ln[N/(N-K)] = 1 \text{ and } K/N \equiv (e-1)/e = 0.632, \qquad (17)$$

at large N and e = 2.718. The final aggregate number is N/e and their mean, $M_K = ea$. Eq.(14) gives the limiting values:

$$b_K = (N-K)\{b_o+2\ln[N/(N-K)]\}/N \equiv (b_o+2)/e, \qquad (18)$$
$$\eta_K \equiv [(b_o+2)/e -1]^{0.5} = [(\eta_o^2+3)/e -1]^{0.5}. \qquad (19)$$

At the initial VC, $\eta_o = 0$, the $\eta_K = [(3-e)/e]^{0.5} = 0.32$. Higher distribution moments are close to those of LND. The t_K value is $(t + 3 + 27^{0.5})/e^2$, or 1.35 for mobile particles identical in their size (1.34 for the LND with $\eta = 0.32$). The simulated fourth moment, c, differed by 1,5% only from its LND value. With initial identical particles, $\sigma_{ln} \approx [\ln(\eta^2+3) - -1]^{0.5} = 0.31$, close to directly calculated 0.29.

A computer simulation has shown the particle size region of considerable probability to be narrow (Fig. 3a). Most of initial particles form little-particle aggregates. If not only initial particles but also small aggregates are mobile, the mean is $M_k = 1+ n_m(e-1)$ where n_m is the largest size of mobile aggregate. The other normalized moments vary slightly. For instance, σ_{ln} is 0.31 and 0.32 at n_m = 2 and 3. If n-aggregates move much faster than (n - 1)-aggregates, and start collide to a considerable degree after all the latter has vanished, the distribution is identical to that formed by simultaneous condensation of all the aggregates up to n_m in size.

In the metal island films whose growth was assumed earlier to occur through the „single-atomic" transfer[22,23] the stable LS about 0.3 was observed at much larger mean particle sizes suggesting the mass transfer also by polyatomic clusters under the conditions of strong metal heating to evaporate. The stable LS value kept in the well-stabilized metal soles also at very large mean particle size[24].

Monodisperse Silver Halide Photographic Emulsions

The last particle size distribution has been recently shown[21] to be compatible with the properties of latent image centers. The mechanisms for their formation assume mobile silver atoms[34] or, what is the same as concerns the process above, such their fragments as photoelectrons and interstitial silver cations[35]. The silver halide surface as the largest microcrystal dislocation[36,37] favors the generation and mobility of photoelectrons[38] as well as binding the photolytic halogen. The latent image distribution simulated is hardly distinguished on the PL scale from a LND with $\sigma_{ln} = 0.3$, even without taking into account the „subcritical" ($n = 2$ and 3) ones (Fig. 3b).

The same stable LS was established by Klein[33] for developed silver particles within the wide exposure range considered. The LS value kept unchanged for grains several orders magnitude larger than initial latent image centers since their development as it was recently shown is a simple linear catalytic reaction occurring at a constant rate[39].

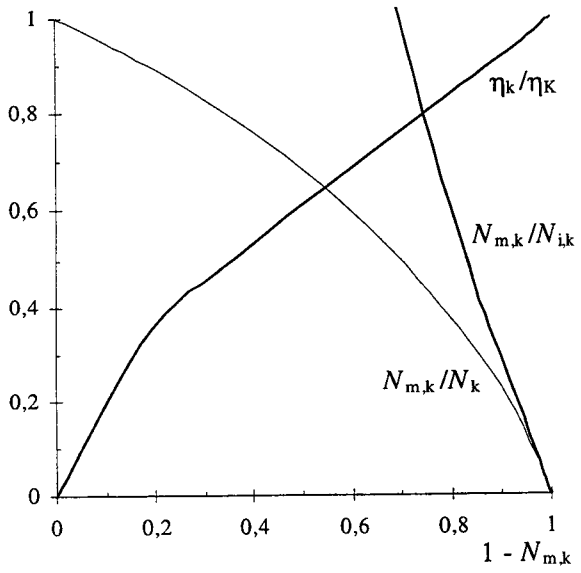

Figure 4. Dependencies of nucleus size VC related to its maximum value, the probability ratio of creating a new nucleus to growing an existing one, and the mobile particles portion on the portion of initial particles spent in the course of nucleation.

The double-jet precipitation conditions are similar as regards to the process statistics. In the presence of gelatin, the probability of polymolecular nuclei to interact one another should be much lower than that of ions to interact one another or the nuclei. Their gelatin shells efficiently prevent a silver halide crystallite to coalesce with another one like in the highly stabilized metal hydrosols[24].

"Gelatin exerts a special power as a protective colloid, for it can totally inhibit crystallization as well as merely suppress growth... Ordinarily, potassium bromide and silver nitrate in one-hundredth normal solution yield a cloudiness immediately on mixing. In the presence of gelatin, even tenth normal solutions give a clear yellow colloidal suspension of silver bromide, which remains transparent for some time... An obvious deduction, and one substantiated by experiment, is that regular crystalline precipitates can be obtained only when the gelatin solutions are stirred... The structure is mechanically broken (and probably instantly mended), and the crystals are nourished by forced convection currents[40]." Organic molecules two times larger in radius than monatomic particles, including halide ions, also move an order magnitude slower in swollen gelatin[41]. Even the 2-molecular silver halide clusters are twice as much in their volume.

The interstitial silver ions are always available in silver halide to complete a silver atom. Thus, the mobile photoelectrons can be quite considered as complete silver atoms in the statistics of the latent image formation[21]. Bromide ions excessive in the solutions for emulsion preparation also cannot have a perceptible effect on the necessary probabilistic condition to hold. They are also always available to complete the provisory silver halide molecules to those actual. The mobility and combining capability of silver ions is obviously the highest one among all the silver-containing particles. The nucleation stage can be reduced to the condensation statistics above with the provisory or actual silver halide molecules only interacting one another or their larger aggregates.

The experimental microcrystal radius VC of 0.08 to 0.12 corresponds to the volume LS about 0.3, characteristic to the probabilistic process under consideration. Its computer simulation gave the VC of 0.095. If the 2-particle aggregates arisen had not grown later, the VC would have decreased to 0.065 that is not observed. If 2-aggregates could also stick one another like simple initial particles, the radius VC would be 0.105. If still 3-aggregates could interact one another, the VC would be 0.11. At higher sticking limit, n_m, the VC are not meet the experimental data available.

An initially attained supersaturation has provided the provisory silver halide molecules to interact each other and produce salt nuclei with a high probability. It is rapidly exhausted in course of nucleation that soon arrests itself (Fig. 4). At usually very high N and k, the sticking probabilities of initial particles and nuclei relate each other as

$$N_{m,k}/N_{i,k} \cong -[1 + \ln(1 - k/N)]/\ln(1 - k/N), \qquad (20)$$

$N_{i,k}$ is the number of nuclei appeared in solution after k acts of adding initial particles to one another or to the nuclei. The ratio tends obviously to infinity at the initial supersaturation and later it decreases to unity when about 2/3 initial particles is spent. The ratio tends then several times faster to 0 than the remained portion of initial particles, $N_{m,k}$ /N. The formation of new nuclei should practically stop when the probability of a new nucleus to arise is at least 10 times less than the probability of an already existing nucleus to grow.

The nucleation stage finishes and the growth stage begins obviously at a still considerable silver ion concentration. That little influences the nucleus VC, η_i. It is 8% and 1% less only if the concentration of initial particles at the beginning of growth is 10 and 100 times lower than that at the supersaturation stage induced the nucleation. The concentration of nuclei, N_i, then would be about 15 and 200 times larger than the concentration of remained initial particles, $N_{m,k}$ /N.

Too much fast reagent supply by single-jet or even double-jet precipitation[40] can repeat at once the supersaturation state and produce polydisperse emulsions whose size distribution is a composition[1] of the nucleation waves. During a monodisperse emulsion preparation, a sufficiently slow supply of reagents prevents the additional nucleation.

On the general probabilistic grounds, a dynamic linear transform of the initial distribution (like that in the latent image development[39]) is necessary, for the initial VC (or LS) value not to vary during the growth stage. The second necessary condition is that the aggregates arisen at the nucleation stage should control the constant rate of the linear mass growth of microcrystal:

$$dm_s / d\,t = kn, \quad \text{and} \quad m_s = kn\,(t - t_o), \qquad (21)$$

t_o is the beginning the growth stage. The transform only provides the particle mean size and standard deviation to vary in proportion to the growth time and to their values after nucleation, thus keeping their constant ratio, VC. Were the mass increments statistically proportional to a particle actual size in the moment, as to Granqvist and Buhrman[2], a proper LND would have arisen with continuously increasing VC.

Crystal growth is commonly assumed to occur with a predominant efficiency through developing helical dislocations. Their active sites may be the nuclei arisen and stabilized in statu nascendi by gelatin at the nucleation stage. The stabilized little-particle clusters may possess a special catalytic activity in growth process due to their strongly distorted quasi-crystalline structure. The nucleus size distribution transforms into an apparently continuous microcrystal size distribution simulating a LND with the same LS and VC.

The characteristic distribution properties are independent of kinetics factors since all the expressions related do not contain a time variable. The finding seems to be of general fundamental importance for the nucleation processes of new condensed phases, including the precipitation of the photographic emulsions.

Summary

1. A mathematical procedure has been proposed and illustrated to derive size distribution functions or their moments. It considers an initial sequence of their elementary variations due to inter-particle collisions and assumes every increment in n-particle aggregates as equal to its probability.

2. Unlike the common idea of lognormal distribution as if appeared in forming a condensed phase, other distribution functions actually arise with stable log-size standard, or size variation coefficient as their inherent mathematical property. They efficiently simulate the lognormal one, thus often misleading of actual mechanisms for the processes. An example is the classic free coagulation that forms a Weibull radius distribution with its unique log-size standard that shows no preference in silver halide emulsions.

3. Another distribution with the stable log-radius standard and radius variation coefficient about 0.1 is shown to be produced by random adding the smallest particles to each other or to their aggregates that cannot interact one another. It is observed at early stages of thin film formation, in highly stabilized metal soles, and corresponds to the main properties of latent image centers as well as to the microcrystal size statistics in monodisperse photographic emulsions.

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