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SIZE DISTRIBUTIONS FOR ULTRAFINE METAL PARTICLES

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Résumé. — La croissance de particules par coalescence est décrite comme une séquence d'événements binaires où, à chaque étape, le changement de volume est une fraction arbitraire du volume après la coalescence. Le modèle prédit que le logarithme de la taille des particules a une distribution Gaussienne. Ceci est supporté par des résultats expérimentaux pour des particules préparées par évaporation dans un gaz inerte, et par la croissance des cristallites dans les couches discontinues et dans les catalystes supportées.

Abstract. — Coalescence growth of particles is described as a sequence of binary events, where at each step the change of volume is a random fraction of the volume after coalescence. The model predicts that the logarithm of the particle size should have a Gaussian distribution. This is corroborated by experimental data for inert gas evaporated particles, islands in discontinuous films and supported metal catalysts.

The growth of a fine metal particle can proceed via two principally different mechanisms : First, collision of grains accompanied by their coalescence can lead to increased sizes. Second, the coarsening can occur by single atom (or molecule) migration between separate particles. In this report I will develop a simple statistical model for coalescence growth. Its most salient feature is the prediction of log-normal size distributions, which will be seen to agree with many experimental size distributions for inert gas evaporated particles, islands in discontinuous films and supported metal catalysts.

To obtain a theoretical description [1, 2] of coalescence the particle growth is considered to take place as a sequence of discrete events, being *binary collisions,* such that one can study the process after any finite number of steps $j = 1,2,\ldots$ The basic assumption is that *the change of volume at each step is a random fraction of the volume after coalescence,* i.e.

$$V_j - V_{j-1} = \varepsilon_j V_j , \tag{1}$$

where $\{\varepsilon_j\}$ is a set of mutually independent random variables, which are not functions of the volumes. Hence, after j collisions one gets

$$V_j = V_0 \prod_{k=1}^{j} (1 - \varepsilon_k)^{-1} , \tag{2}$$

where V_0 denotes the initial volume. By taking the logarithm of eq. (2) it is seen that $\ln(V_j/V_0)$ is a sum of positive and independent random variables each with the same probability distribution, and it follows from the Central Limit Theorem [3] of mathematical statistics that this quantity is, *asymptotically,* a Gaussian. Hence, in the limit of many coalescence events the particle volumes have a *log-normal distribution function* (L.N.D.F.) [4]. A more detailed derivation is given in reference 2. The number of particles Δn per logarithmic volume interval $\Delta(\ln v)$ can be written $\Delta n = f_{\mathrm{LN}}(v)\,\Delta(\ln v)$ with

$$f_{\mathrm{LN}}(v) = \frac{1}{(2\pi)^{1/2} \ln \sigma_v} \exp\left\{ -\frac{1}{2}\left[\frac{\ln(v/\bar{v})}{\ln \sigma_v}\right]^2 \right\} , \tag{3}$$

where $\bar{v}$ is the statistical median of the volumes and σ_v is their (geometric) standard deviation.

For the special case of spheres one has the normalized distribution

$$f_{\mathrm{LN}}(x) = \frac{1}{(2\pi)^{1/2} \ln \sigma} \exp\left\{ -\frac{1}{2}\left[\frac{\ln(x/\bar{x})}{\ln \sigma}\right]^2 \right\} \tag{4}$$

for the diameters x. Here $\bar{x}$ denotes the median diameter, which is related to $\bar{v}$ by

$$\bar{x} = (6/\pi)^{1/3}\, \bar{v}^{1/3} , \tag{5}$$

and σ is the geometric standard deviation of the diameters, which is given by

$$\sigma = \sigma_v^{1/3} . \tag{6}$$

For ellipsoidal particles it follows from the multiplicative reproductive properties [4] of the L.N.D.F. that a relation analogous to eq. (4) should be obeyed for each of the three perpendicular axes, provided these are statistically independent. To illustrate the applicability of the L.N.D.F. eq. (4) will now be confronted with experimental data pertaining to particles produced by various experimental techniques.

Inert gas evaporation has been widely used to prepare ultrafine particles. The simplest technique is to vaporize a metal in a vacuum plant containing a reduced atmosphere of a noble gas [5-7]. To improve the particle yield and keep the evaporation

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rate constant we recently used a temperature stabilized oven as vapour source [2]; by this method we were able to prepare sizable amounts (grams) of well characterized particles having median diameters down to below 3 nm. An alternative technique to enhance the particle yield is to use a plasma jet flame as vapour source [8]. Common to these techniques is that atoms, which are effused from the heated metal, lose their energy rapidly by collisions with gas atoms. A highly supersaturated state is then reached, from which stable clusters of metal atoms are produced by homogeneous nucleation. These embryonic particles grow to form larger grains, whose ultimate size is governed by several experimentally accessible parameters like evaporation rate, atomic (or molecular) weight of the gas, its pressure etc. The most natural assumption for the growth mechanism is that colliding particles coalesce. This process is supposed to be rapid due to melting point depression in minute particles as well as heating provided by the vapour source. The statistical model above now leads to the prediction that experimental size distributions should obey L.N.D.F.'s. This is indeed in accordance with electron microscopic evidence as proved in figure 1, where the specimen was prepared by evaporation from a temperature stabilized oven. To achieve the correct normalization of the L.N.D.F. $\sum_i n_i(\Delta x/x) f_{\mathrm{LN}}(x)$ *versus* x is plotted in the figure. Here $\sum_i n_i$ is the total number of particles in the sampling. Δx is the width of the staples in the experimental histogram. The standard deviations for the evaluation in figure 1 fall within the interval

$$\sigma = 1.48 \pm 0.12\,,$$

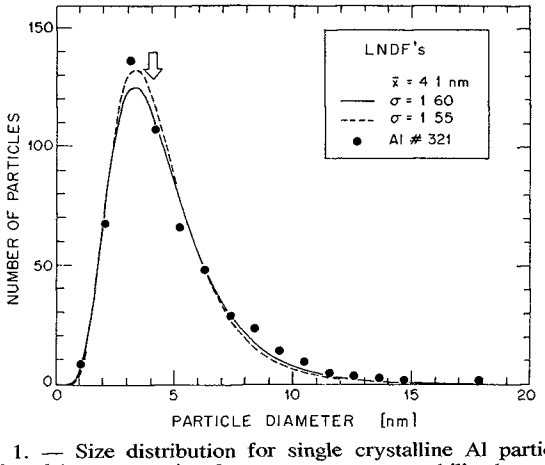

FIG. 1. — Size distribution for single crystalline Al particles produced by evaporation from a temperature stabilized oven in an atmosphere of 3.5 torr of Ar. A small amount of O_2 was admitted continuously to the inert gas in order to give a dielectric coating on the individual grains. A random sampling of the specimens was investigated with an AEI type EM 802 electron microscope operating at 80 kV in dark field mode. The filled circles denote midpoints in a size histogram with $\Delta x = 1.05$ nm and $\sum_i n_i = 518$. The curves show L.N.D.F.'s as defined by eq. (4) with $\bar{x}$ and σ given in the figure. The location of $\bar{x}$ is indicated by an arrow.

as was found to occur consistently in our previous extensive investigation [2] of inert gas evaporated particles.

Island coarsening in a discontinuous film gives another example of coalescence growth. The accepted view of metal film build-up is that the deposit goes through a number of distinct stages. First nucleation occurs on the substrate surface. Further deposition makes these nuclei grow via impingement or surface diffusion of single atoms. Depending on substrate conditions and nuclei density the discontinuous film may then enter a stage where coalescence is the dominant growth mechanism. Finally the islands grow together to form a continuous layer. Recently [9] we investigated growth of islands in discontinuous gold films evaporated in U.H.V. onto glass substrates. Films with thicknesses t of 2, 3, 4 and 4.5 nm were prepared. The islands, as seen in the electron microscope, could be well approximated by ellipses (with perpendicular axes a and b) at least for $t \leqslant 4$ nm. Both major and minor axes were generally found to be accurately described by L.N.D.F.'s (defined by $\bar{a}$ and σ_a resp. $\bar{b}$ and σ_b.) as predicted from the above model of coalescence, taking a and b to be statistically independent entities. From the reproductive properties of the L.N.D.F. [4] we then obtain that also the *equivalent projected diameter,* defined by

$$x = (ab)^{1/2}\,, \tag{7}$$

should obey an L.N.D.F. with

$$\bar{x} = (\overline{ab})^{1/2} \tag{8}$$

and

$$\sigma = \exp[\tfrac{1}{2}(\ln^2 \sigma_a + \ln^2 \sigma_b)^{1/2}]\,. \tag{9}$$

Empirically, x displays a log-normal behaviour as shown in figure 2 for four different average film thicknesses. The values of $\bar{x}$ and σ are collected in table I. It is thus seen that the L.N.D.F. remains a good approximation for the experimental size distribution, while $\bar{x}$ varies from 6.5 nm up to 16.5 nm and the number of islands per cm^{-2} is decreased from 8.5×10^{11} to 1.3×10^{11}. The geometric standard deviations fall consistently within the range

$$\sigma = 1.28 \pm 0.06\,,$$

which was found [1, 2] to be typical for islands growing by coalescence in discontinuous noble metal films.

Log-normal size distributions are frequently found also for particles in *supported metal catalysts.* An example is shown in figure 3, where an experimental size distribution for a Pd-Au alloy catalyst, reproduced from Bond [10], is found to be in virtually perfect agreement with eq. (4). This result is of interest for the long-standing problem whether catalyst particles coarsen (and hence loose their catalytic activity) due to coalescence growth or

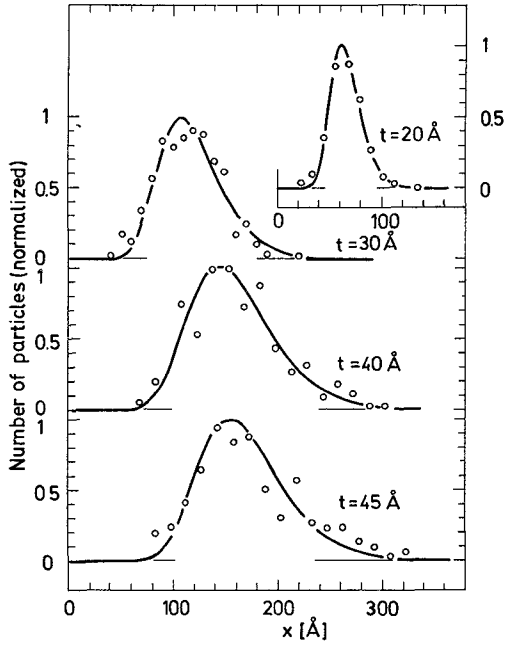

FIG. 2. — Size distributions for islands in discontinuous gold films prepared by evaporation onto Corning 7059 glass substrates at a pressure of $< 4 \times 10^{-9}$ torr (background pressure $< 6 \times 10^{-10}$ torr). An electric field of 20 V/cm was maintained in the substrate plane. After ageing the deposits in U.H.V. for 20 h. a stabilizing carbon layer was deposited on top of the gold films. Subsequently the substrate was dissolved in HF acid and the free films were studied with a Philips EM 300 electron microscope operating at 100 kV in bright field mode. The circles in the figure denote midpoints in histograms based on evaluations of *a* and *b* for 300 islands at each thickness. The curves represent L.N.D.F.'s defined by $\bar{x}$ and σ as given in table I ; they are normalized such that the mode ordinates are assigned the value unity.

TABLE I

Data for discontinuous gold films ; results are given for average film thickness t, median island diameter $\bar{x}$, geometric standard deviation for the islands σ and number of particles per unit area n.

$t \pm 10\%$ [nm]	$\bar{x}$ [nm]	σ	n [10^{11} cm^{-2}]
—	—	—	—
2	6.5	1.25	8.5
3	11.6	1.30	3.8
4	15.5	1.30	1.6
4.5	16.5	1.28	1.3

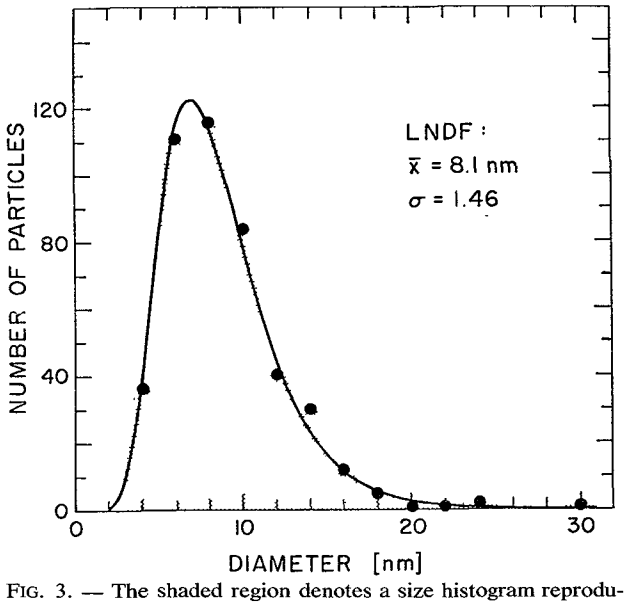

FIG. 3. — The shaded region denotes a size histogram reproduced from figure 4.10 of reference [10]. Staple midpoints are indicated by heavy dots. The fitted curve represents an L.N.D.F. characterized by the shown values of $\bar{x}$ and σ.

Ostwald Ripening. The agreement with the L.N.D.F. clearly speaks strongly in favour of coalescence, as we pointed out recently [11].

In conclusion, I have forwarded a simple statistical model of coalescence growth of particles, which yields that the asymptotic size distributions are log-normal. It should be noticed that no similar statistical derivation of, for example, the Gaussian or Poisson distribution is possible. The prediction of log-normality was verified by comparison with experimental size distributions for inert gas evaporated particles, islands in discontinuous films and supported catalysts. The good correspondence can be taken as evidence for the soundness of the basic assumptions at the beginning of this paper. The present report summarizes results discussed at length in references [1, 2, 9 and 11].

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