Ultrafine metal particles

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(Received 19 November 1975)

In this paper we present a novel and versatile technique for the production of ultrafine metal particles by evaporation from a temperature-regulated oven containing a reduced atmosphere of an inert gas. An extensive investigation of particles of oxidized Al, with diameters of 3 to 6 nm, has been performed. We have also studied ultrafine particles of Mg, Zn, and Sn produced in the same manner. A supplementing investigation has been carried out for particles of Cr, Fe, Co, Ni, Cu, and Ga, as well as larger Al particles, produced by "conventional" inert-gas evaporation from a resistive filament. Diameter as a function of evaporation rate, inert-gas pressure, and the kind of inert gas are reported. Crystalline particles smaller than 20 nm look almost spherical in the electron microscope, while larger ones often display pronounced crystal habit. Size distributions have been investigated in detail, and consistently the logarithm of the particle diameter has a Gaussian distribution to a high precision for the smallest sizes, whereas larger particles deviate from such a simple behavior. A statistical growth model, based on the Central Limit Theorem, has been formulated for liquid-like coalescence of particles; this theory accounts satisfactorily for all our data, as well as for most size distributions published in the literature. Applications of the model to colloids, discontinuous films, and supported catalysts are discussed. By comparing size distributions for particles produced by a variety of techniques we found a number of empirical rules for the width of the distributions, as defined by a (geometric) standard deviation $\sigma$. For crystalline inert-gas-evaporated particles we obtained consistently $1.36 < \sigma < 1.60$; for coalescing islands in discontinuous films we found $1.22 < \sigma < 1.34$, and similar rules are applicable to colloids, supported catalysts, and to ultrafine droplets.

PACS numbers: 81.60.+k, 06.60.Ei, 61.50.Cj, 81.20.-n

I. INTRODUCTION

In Sec. II of this paper we describe a versatile technique, based on inert-gas evaporation, to produce ultrafine metal particles with medium diameters down to below 3 nm in amounts of the order of grams. A typical size histogram is depicted in Fig. 1. We then discuss at length the electron microscopic analysis of the particle sizes and show that a log-normal distribution function (LNDF) is obeyed to a high accuracy for sufficiently small particles. In the following paper we demonstrate that LNDF's can be extracted also by computation from measurements of field-dependent magnetization of small superconducting particles. In Sec. VI we discuss a number of empirical rules pertaining to the widths of size distributions for particles produced by different techniques; as an example, the geometric standard deviation $\sigma$ for inert-gas-evaporated particles is invariably in the range $1.36 < \sigma < 1.60$. The novel experimental technique, as well as the analytic form of the size distribution and the empirical rules for the distribution widths, should be of considerable interest in connection with experiments on the properties of ultrafine matter.

A glance through the recent literature reveals a substantial interest in the physics of minute metal particles. For sizes being sufficiently small to produce measurable splittings of the energy bands there have lately been measurements of magnetic susceptibility, far-infrared transmission, and nuclear magnetic resonance. Shifted plasma resonances have been probed by optical means. Modified vibrational properties have been investigated by specific-heat measurements, the Mössbauer effect, and by electron and x-ray diffraction from ultrafine particles. Altered superconducting transition temperatures and "zero-dimensional" fluctuations of the order parameter have been studied. For most of these experiments it is imperative to be able to produce quantities of particles of controlled size and to know the particle sizes accurately. The listing is by no means exhaustive, but should suffice to demonstrate the present-day activity in small-particle physics and the potential significance of the present work. Preliminary accounts of some aspects of our experiments have been reported in Refs. 15 and 16.

The plan of this paper is as follows: In Sec. II we discuss various techniques to produce ultrafine metal particles and argue that, in several respects, the best

FIG. 1. Size histogram for oxide-coated Al particles. The staples represent a random sampling of a specimen weighing more than 1 g. The statistical median diameter, as determined by dark-field microscopy, is slightly above 4 nm. The asymmetric bell shape and the tail toward larger diameters are characteristic features of the log-normal distribution. Sample Al No. 321 will be analyzed in detail in Figs. 3, 9, 10(a), and 12 below.
method is inert-gas evaporation using a temperature-stabilized oven as a vapor source. Our experimental setup is described. Section III reports on our electron microscope studies of the external shapes and the crystal structures of Mg, Al, Cr, Fe, Co, Ni, Cu, Zn, Ga, and Sn particles. In Sec. IV we discuss nucleation and growth of ultrafine particles and present our measurements of particle size as a function of evaporation conditions. The most important result of our growth model, based on liquidlike coalescence of particles, is the prediction of an LNDF for the particle sizes. This distribution function is then compared with a large quantity of experimental data in Sec. V, and we demonstrate that the LNDF is obeyed very well for particles which do not display crystal habit, in which case the fit is considerably poorer. Section VI provides a review of size distributions, mainly, as compiled from the literature, for particles produced by colloid chemical techniques, island growth in discontinuous films, and methods to make supported metal catalysts. Comparison of these methods with inert-gas evaporation shows that the distribution width is predominantly a function of the general method used to prepare the particles (e.g., inert-gas evaporation, island formation in discontinuous films, etc.) rather than the detailed conditions for particle growth within each specific method. The major results and conclusions are summarized in Sec. VII. The reference list is made rather extensive and, until a more complete survey of various particle fabrication techniques becomes available, we hope that this work may also serve as a brief review of the subject.

II. PRODUCTION OF ULTRAFINE METAL PARTICLES

A critical discussion of several methods to produce ultrafine metal particles is followed by a description of our inert-gas-evaporation technique using a temperature-stabilized oven as a vapor source.

A. Critical survey of methods to make ultrafine particles

Generally speaking, the particle samples should fulfill four criteria in order to permit meaningful measurements of many of the physical properties listed in the second paragraph of Sec. I:

(i) the mean particle size should not be larger than approximately 10 nm;
(ii) the distribution of particle sizes should be narrow and, more important, be accurately known;
(iii) the individual particles should be electrically insulated from one another;
(iv) the samples should be sufficiently large (often implying a weight of 0.1 to 1.0 g).

A large number of experimental techniques to produce ultrafine metal particles has been put forward in the literature. Unfortunately, most of these are restricted to only a few particular materials, as for example, the methods\textsuperscript{17,18} to make noble-metal colloids (we return to these in Sec. VI A), gold or silver granules in a photosensitive glass,\textsuperscript{19,20} or alkali-metal particles in an alkali halide matrix.\textsuperscript{21,22}

A much more versatile technique is the Stedberg electrochemical method\textsuperscript{23-25} which consists of striking high-frequency electrical arcs between metal chips under either a polar liquid or a nonpolar liquid containing a protective colloidal agent. The vaporized material (which can be a refractory metal) condenses in the liquid and goes into suspension as tiny colloidal particles. Experimentally it is commonly found that at least requirements (i) and (iii) above can be difficult to fulfill, and also spurious effects from traces of the liquid may hamper an interpretation of results obtained with particles produced in this manner. An additional drawback for many experiments is the fact that the particles are usually polycrystalline.

The discontinuous multilayer technique has recently\textsuperscript{8,26} received some attention. Here several layers are deposited on top of each other; every second layer is a metal film in its “island stage” of growth, while the rest of the sample is composed of insulating continuous films. (A detailed discussion of island growth follows in Secs. VI B–VI E.) With the technique criteria (ii) and (iv) are especially difficult to achieve.

![Cross-sectional sketch of the experimental setup to produce ultrafine metal particles by inert-gas evaporation from a temperature-controlled oven. The apparatus is described in the main text.](image)

**FIG. 2.** Cross-sectional sketch of the experimental setup to produce ultrafine metal particles by inert-gas evaporation from a temperature-controlled oven. The apparatus is described in the main text.
In many respects the best way of making ultrafine metal particles is by \textit{inert-gas evaporation}, where nucleation and growth takes place in a noble-gas atmosphere. The technique was pioneered by Pfund,\textsuperscript{27} Burger and van Cittert,\textsuperscript{28} and by Harris \textit{et al.},\textsuperscript{29} It has subsequently been used extensively.\textsuperscript{30-40} Proper selection of the kind of gas, its pressure, and the evaporation rate has allowed production of specimens fulfilling requirements (i) and (ii). For those materials whose particles grow a dielectric oxide coating it would have been possible to achieve (iii) as well, though this has not been widely exploited. Precautions were generally not taken to keep the resistive filament vapor source at constant temperature, and thus the evaporation rate and consequently the average particle size could vary during evaporation. Furthermore, experimental samples usually originated from several different evaporation processes, since a resistive filament can carry only a small metal charge. To overcome these difficulties we developed a technique where the vapor is produced by heating a large quantity of material in a temperature-stabilized oven.

\section*{B. Inert-gas evaporation using a temperature-controlled source}

Figure 2 is a somewhat schematic picture of the apparatus for making ultrafine metal particles by well-controlled evaporation from an oven. A large glass cylinder (diameter 0.34 m, height 0.45 m), fitted to water-cooled stainless-steel endplates, could be evacuated to a pressure of approximately $2 \times 10^{-6}$ Torr by an oil diffusion pump. A crucible (high-purity re-crystallized alumina), placed on a stand-off, was slowly heated via radiation from a graphite heater element. The temperature sensor was a Pt-PtRh thermocouple connected to the temperature-regulating unit of a power supply (maximum 20 kW) for the heater; the temperature could be kept at a preset value to within a few degrees centigrade for any length of time. After an appropriate outgassing the pumping line was closed and a reduced atmosphere of an inert gas, usually 0.5-4 Torr of argon (99.999\% purity), was introduced into the cylinder. The crucible was now heated rapidly under quasiequilibrium conditions (constant temperature and inert-gas pressure), the large lid, which previously had covered the main part of the cooling plate, was put in its vertical position (cf. Fig. 2) by turning the L-shaped rod operated via the rotary feedthrough extending through the top plate. The particles, which nucleate and grow in the gas, now were collected on the water-cooled surface.

Many evaporation of Al have been performed. With this material it was easy to make the particles electrically decoupled from one another by bleeding in oxygen during the evaporation to grow an insulating coating of Al$_2$O$_3$. By use of a flow impedance of porous copper we admitted a few cm$^3$/min of O$_2$; the flow rate was easily changed by adjusting the pressure regulator on the O$_2$ cylinder.

At the highest attainable temperatures (approximately 1600°C at an inert-gas pressure of a few Torr) the thermocouple did not give reliable readings, but a satisfactory temperature measurement was obtained by an optical pyrometer looking down into the crucible. Gas convection prevented any significant amount of particles from sticking to the glass cylinder near the edges of the cooling plate, and hence pyrometry could be carried out in a straightforward manner (cf. Fig. 2).

To check the particle sizes an electron microscope grid covered by a carbon film was attached to the center of the cooled surface. A small shutter, operated from the top vacuum plate, made it possible to sample less than a monolayer of particles on the grid, even when the deposit on the rest of the cooling plate was many times thicker. When an appropriate quantity of ultrafine particles had been produced the big lid was brought back to its initial (horizontal) position and the heat was turned down. After disassembling the vacuum system the particles were collected by brushing them off the cooling plate.

In the above manner we have produced and studied more than 20 samples of Al and a smaller number of samples of Mg, Zn, and Sn. In addition, we have produced ultrafine particles of Cr, Fe, Co, Ni, Cu, and Ga in a more conventional way: by inert-gas evaporation from a tungsten filament in a bell-jar system and collecting the particles on a glass surface partially surrounding the vapor source.

\section*{III. ELECTRON MICROSCOPY}

A brief description of the preparation of samples for electron microscopic studies is followed by a discussion of the shapes and crystal structures of the ultrafine particles.

\section*{A. Sample preparation}

As described in Sec. II, a microscope grid could be exposed briefly during the evaporation of a large amount of material within a few minutes. By use of a flow impedance of porous copper we admitted a few cm$^3$/min of O$_2$; the flow rate was easily changed by adjusting the pressure regulator on the O$_2$ cylinder. The temperature sensor was a Pt-PtRh thermocouple connected to the temperature-regulating unit of a power supply (maximum 20 kW) for the heater; the temperature could be kept at a preset value to within a few degrees centigrade for any length of time. After an appropriate outgassing the pumping line was closed and a reduced atmosphere of an inert gas, usually 0.5-4 Torr of argon (99.999\% purity), was introduced into the cylinder. The crucible was now heated rapidly under quasiequilibrium conditions (constant temperature and inert-gas pressure), the large lid, which previously had covered the main part of the cooling plate, was put in its vertical position (cf. Fig. 2) by turning the L-shaped rod operated via the rotary feedthrough extending through the top plate. The particles, which nucleate and grow in the gas, now were collected on the water-cooled surface.

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FIG. 4. Bright-field images of large particles. (a) shows Al particles which are much bigger than those of Fig. 3. They were produced by evaporation at $p(\text{Ar}) = 15$ Torr in the bell-jar system. A tendency towards hexagonal shapes can be seen in agreement with observations in Refs. 34–36; a detailed study of Al particles was reported in Ref. 37. The very large Mg particles in (b) were made by oven evaporation at a source temperature of 845°C and at $p(\text{Ar}) = 3.5$ Torr. They are either thin hexagonal plates or "butterfly"-shaped hexagons. These findings agree with the extensive investigation of Ref. 38 as well as the observations in Refs. 32 and 34–36. Pictures of Zn particles are given in (c). The particles were produced at $p(\text{Ar}) = 3.5$ Torr and an oven temperature of 975°C; they look either like hexagons or like more or less irregular "butterflies". Our results are in agreement with those of Refs. 34–36 and 39–41. (d) shows particles of bcc Cr produced by filament evaporation in $p(\text{Xe+air}) = 1.5 \pm 0.1$ Torr. The almost perfectly cubic shape of the larger particles has been noted earlier in Ref. 42. Small Fe particles are depicted in (e), the most salient feature being the "necklace" formation. This is generally observed for magnetic particles as discussed in the main text. The crystallite shape is probably a rhombic dodecahedron (cf. Ref. 34). The particles were produced by filament evaporation at $p(\text{Ar}) = 10$ Torr. (f), finally, shows Ga particles (drops) made in the bell-jar system at $p(\text{Ar}) = 10$ Torr. The perfectly spherical shape was observed also in Ref. 34.

of material. This grid was normally put at the center of the cooling plate which, of course, yielded no check on the particle sizes in other parts of the collection surface. Although we have performed experiments (cf. Sec. VB, below) to verify that the diameters do not change very much at different spots on the cooling plate, this simple method was not regarded as sufficiently accurate for the careful size distributions reported in Sec. V. Instead we proceeded in the following more complicated manner. When all the particles had been collected the powder sample was thoroughly mixed. A small portion of the powder was suspended in water with ethyl alcohol using an ultrasonic bath. A microscope grid was dipped in the suspension and, after drying, it was ready for viewing. This technique is henceforth called "random sampling".
The specimens were studied with an AEI type EM802 electron microscope with a highest accelerating voltage of 100 kV and a largest magnification on the fluorescent screen of 190,000 diameters. Normally the pictures that were taken were magnified photographically 3–6 times before any evaluation of the sizes commenced.

B. Shapes and crystal structures of the particles

Figure 3(a) shows a bright-field image of a random sampling of our specimen Al No. 321 for which the size histogram was given in Fig. 1. It is evident that the particles stick together in clusters. This is probably an electrostatic effect as well as an artifact of the drying of the aqueous suspension. A less-pronounced tendency for clustering was found for particles collected on a grid attached to the cooling plate. The clustering clearly makes an evaluation of the size distribution troublesome, but the problem can be evaded to some extent by going to dark-field microscopy which is a selective technique in the sense that only those particles contribute to a small portion of the diffraction rings (as picked out by an aperture) yield any contrast; this is shown in Fig. 3(b). The dark-field mode of operation has been used whenever very careful size distributions were demanded. For Al particles a combination of bright-field and dark-field techniques allowed a determination of oxide thicknesses as discussed in Sec. V C below. For unoxidized particles dark-field and bright-field sizes agreed well with one another.

Size determination by dark-field microscopy requires single-crystalline particles. Experimentally we have found this to be the case even for diameters on the micron scale. Only exceptionally have we found particles composed of two crystallites.

The tiny Al particles of Fig. 3 look almost spherical, and this is equally true, irrespective of constituent elements, for all inert-gas-evaporated particles smaller than about 20 nm. For larger sizes, however, the picture is quite different and distinct crystal habit is normally seen as evidenced by Figs. 4(a)–4(e). According to the Gibbs-Wulff relation the external shape is governed by

$$\sum_i \xi_i A_i = \text{minimum},$$

where $\xi_i$ is the specific surface free energy of the $i$th face, whose area is $A_i$. This criterion predicts polyhedral shapes for crystalline particles which, empirically, agrees with our observations on particles with diameters exceeding 20 nm, but apparently fails for the smallest sizes.

Magnetic particles (Fe) are shown in Fig. 4(e). The long chains, being a manifestation of the magnetic interaction, are characteristic for all our samples of Fe, Co, and Ni, as well as for all data in the literature on such particles. The smallest magnetic particles, having median diameters about 3 nm, seemed to display a less pronounced tendency to form chains.

Electron diffraction showed that all of our inert-gas-evaporated particles were crystalline with the exception of Ga, which yielded only diffuse halos signifying an amorphous material. Actually, the Ga particles of Fig. 4(f) consist of supercooled liquid. In the absence of a long-range crystal structure the Gibbs-Wulff criterion (where now $\xi_i = \xi$ represents the surface tension) predicts a spherical shape which is also found experimentally even for the largest particles.

Abnormal crystal structure was found for Cr, which crystallized in a metastable A15-type atomic arrangement when evaporated in a very clean atmosphere of Ar or Xe, as first reported by Kimoto and Nishida. When a small amount of oxygen was present during the evaporation only the normal bcc phase was obtained [cf. Fig. 4(d)], presumably due to heating caused by the strongly exothermic nature of chemisorption of O$_2$ onto the surfaces. Our experiments on A15-type particles have been reported separately. The A15 structure has been found also as a high-temperature phase of pure Cr in bulk form, and evidently the new structure is found as a metastable phase due to the very rapid quenching of the Cr particles in the gas. An analogous behavior was found for Co, where the particles had an fcc structure. Evidently the high-temperature fcc phase, which only is stable above 450°C in bulk specimens, can be maintained to below room temperature in small enough particles. One may compare this result with reported x-ray measurements on fine-grained Co sponge, where the fcc phase was stable at room temperature. It is worth pointing out that small particles of γ-iron (fcc), as found recently, can be explained in the same way; however no trace of the γ structure was detected in our Fe particles, which is probably due to our slow evaporation rates, i.e., low source temperatures. A15 Cr, fcc Fe, and fcc Co all represent good examples of the phenomenological Ostwald rule which states that in the course of going from a nonequilibrium phase to a final equilibrium state, the system will pass stepwise through states of intermediate stability.

Diffraction lines due to oxides were found only in two cases in the present work: for Fe$_2$O$_3$ and for Cu$_2$O. The oxide formed on the iron particles even when these were produced under the cleanest possible conditions. It is interesting to note that thick oxide coatings of Al particles yielded nothing but highly diffuse scattering of the electrons; evidently the oxide is amorphous.

The color of most of the particles, including unoxidized Al, was black; exceptions were Mg, Zn, and Ga which formed grey deposits and thick Cu layers which were very dark red. For Al we found that the color changed from greyish brown for oxide-coated particles to very light brown for particles consisting entirely of Al$_2$O$_3$.

IV. GROWTH OF INERT-GAS-EVAPORATED PARTICLES

In this section we first describe briefly (Sec. IV A) homogeneous nucleation of particles as the metal vapor is cooled. The subsequent growth, normally taking place in a layer above the hot metal surface, is discussed in Sec. IV B, where we also present our measurements of particle diameter as a function of evaporation parameters. A statistical theory for liquidlike
coalescence of particles is formulated in Sec. IV C; most salient is the prediction of a log-normal distribution of particle volume. This statistical distribution is discussed in Sec. IV D. Some comments on growth by absorption of atomic vapor are given in Sec. IV E.

A. Homogeneous nucleation

In the inert-gas-evaporation process the metal atoms effused from the source will rapidly lose their energy by collisions with gas atoms, i.e., macroscopically the metal vapor is cooled in the gas. The collision mean free path is very short indeed; for Al atoms in 1 Torr of Ar, for example, it is approximately $10^{-7}$ m. This efficient cooling produces locally a high supersaturation of metal vapor\(^{57,58}\) which leads to a homogeneous nucleation.\(^{59,60}\)

The “critical diameter” $x_{\text{crit}}$, for the spontaneously formed embryonic particles is given from simple equilibrium thermodynamics, which is sufficient for our purposes, by\(^{60}\)

$$x_{\text{crit}} = 4 \pi \rho R T \ln \left( \frac{\rho_i}{\rho_0} \right)^{1/3},$$

(2)

where $\rho$ is the density, $R$ is the gas constant for the metal vapor of absolute temperature $T$, and $\rho_i/\rho_0$ represents the supersaturation ratio, i.e., the true vapor pressure (determined by the source temperature $T_0$) divided by the equilibrium vapor pressure at the actual temperature. The point we want to stress here is that due to the rapid cooling of the metal vapor $x_{\text{crit}}$ is expected to be extremely small. As an example Fig. 5 shows the critical diameter versus temperature fall off relative to the source temperature in the case of Al vapor. It is evident that after cooling the Al vapor a few hundred degrees $x_{\text{crit}}$ is of the order of atomic dimensions. From this small value it follows that the free-energy barrier against nucleation, being $\frac{1}{3} \pi x_{\text{crit}}^3$, can readily be exceeded.

![Fig. 6. Conceptual model for particle growth. For most materials nucleation and growth takes place only in a region (thickness $\delta$) above the metal surface. In the rest of the glass cylinder or bell jar the crystalline particles are carried by convective gas flow.](image)

B. Growth layer

Once the nucleation has taken place the growth stage begins. Excepting Ga (cf. Fig. 4(f)) and Se particles (cf. Refs. 34 and 39) which remain liquid to room temperature, we believe that this growth occurs only in a layer above the surface of the hot metal; this is shown schematically in Fig. 6. A priori, the layer thickness $\delta$ is determined by the availability of atomic vapor, or

![Fig. 7. Median particle diameter versus vapor pressure at the metal surface, or source temperature, for Mg and Zn evaporated under two different argon pressures (2.5 and 3.5 Torr). The thermocouple was clamped to the bottom of the alumina crucible (cf. Fig. 2) which should ensure an acceptable thermal connection with the liquid metal, and we believe the thermometer readings to be accurate to $\pm 5$ K. The error bars denote the uncertainties in the size determination and in the empirical relation (Ref. 61) between source temperature and vapor pressure.](image)
by the temperature of the particles being so high that they behave as liquid, whichever of these yields the largest δ. In the former case impinging atoms can be bound to the surfaces of the growing particles; in the latter case particles can coalesce. We believe that coalescence is the dominant growth mechanism, and we will see in the rest of the paper that one can obtain a consistent description of all size distributions for ultrafine particles without invoking absorption of atomic vapor.

It has been reported that larger particles are formed at higher evaporation rates or, equivalently, at higher source temperatures. Our oven evaporation technique allowed us to carry out a quantitative investigation of particle size versus vapor pressure at the hot metal surface. Figure 7 reports measurements for Mg and Zn performed at two different pressures of argon. The agreement among the data for Mg and Zn shows that the metal vapor pressure, rather than the source temperature, is the relevant scaling parameter and that the median particle diameter is proportional to \( p_1 \) to a first approximation.

For growth limited by the existence of liquidlike particles \( \delta \) is expected to be only weakly dependent on the source temperature (cf. the narrow temperature ranges at the upper scales of Fig. 7). However at higher source temperatures the density of particles within the growth layer is larger, so that coalescence occurs more frequently.

Figure 7 also indicates that larger particles are formed at higher inert-gas pressures, as has been pointed out previously. This experimental result is further elaborated on in Fig. 8, which reports on our measurements of particle size as a function of inert-gas pressure and the kind of inert gas (He, Ar, or Xe). It appears that the median diameter is roughly proportional to the pressure for a given kind of gas, and that an increased atomic weight of the gas is favorable for the formation of large particles. These results, we believe, can be explained simply by the higher gas pressure or atomic weight yielding a more efficient confinement of the particles to the growth region in the immediate vicinity of the vapor source.

We found that particles collected closer to the source tended to be somewhat smaller than those condensed farther away. Although this could be taken as evidence for a large growth zone we feel the most likely explanation is that particles which have to be carried a larger distance by the convective gas flow also have a higher probability to reenter the growth layer for some time.

C. Statistical theory of coalescence

In Sec. IV B we treated a number of results that can be understood qualitatively with reference to the existence of a growth layer. In order to go ahead to more detailed predictions the growth process has to be discussed in greater detail. The basic assumption is that only coalescence of particles has to be considered. One can then derive an analytic form of the distribution of particle volumes using concepts similar to those in a rather old statistical “theory of breakage” or in recent turbulence theory.

Underlying the treatment is the notion that particle growth may be conceived of as proceeding via discrete events, i.e., one can logically study the process after any finite number of steps \( j = 1, 2, \ldots \). The initial distribution of particle volumes is called \( F_j(v) \), which represents the proportion of particles with a volume \( v \). These particles are subject to a sequence of independent coalescence processes. If one considers only coalescence of two particles at a time, the volume distribution at the \( j \)th step is given by

\[
F_j(v) = \int_0^v G_j(v, u) d[F_{j-1}(u)],
\]

where \( u \) denotes the volume of one of the particles which combines with another to form a new particle of volume \( v \), and \( G_j(v, u) \) is a function whose form we do not need to specify. The main assumption of the theory is that the change of volume at each coalescence event is a random fraction of the volume after coalescence. At present we do not attempt any explanation of this hypothesis, but leave the statement as an intuitively plausible postulate. The random-fraction requirement may be written as

\[
v - u = \epsilon_j v,
\]

where \( \{\epsilon_j\} \) is a set of independent random variables, which do not depend on the volumes. This implies that only the ratio \( v/u \) enters the problem, and we may define a new function

\[
G_j(v, u) = G_j(v/u).
\]

Inserting this into Eq. (3) we obtain from a well-known theorem for distribution functions that

\[
V_j = T_j V_{j-1},
\]

where \( V_j \) and \( T_j \) are the variables associated with the distribution functions \( F_j(v) \) and \( G_j(l) = G_j(v/u) \). Hence, after \( n \) coalescence steps

\[
V_n = V_0 \prod_{j=1}^n T_j,
\]

where \( V_0 \) denotes the initial volume. Alternatively, Eq. (7) can be written

\[
\ln \frac{V_n}{V_0} = \sum_{j=1}^n T_j,
\]
where from Eq. (4) $\{T_i\}$ is a set of independent random variables each with the same probability distribution. It follows then from the Central Limit Theorem of mathematical statistics that $\ln(V_r/V_0)$ is, asymptotically, Gaussian.

**D. The log-normal distribution function (LNDF)**

The statement that the logarithm of the volume is Gaussian can be written for spherical particles as

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

where $f_{LN}(x)$ denotes the (normalized) log-normal distribution function and $x$ is the particle diameter. The relation follows because a product of LNDF's is still an LNDF. More generally, Eq. (9) is valid for volumes which can be expressed in the form

$$v = ax^b,$$

where $a$ and $b$ are constants specified by the shape of the particles. The parameters $x$ and $\sigma$, which rigidly define the distribution, denote the statistical median and the geometric standard deviation, respectively, as defined by

$$\ln \bar{x} = \sum n_i \ln x_i / (\sum n_i)^{-1}$$

and

$$\ln \sigma = [\sum n_i (\ln x_i - \ln \bar{x})^2 (\sum n_i)^{-1}]^{1/2},$$

where $n_i$ is the number fraction of particles in an interval of the size histogram centered around $x_i$. It should be noted that the geometric standard deviation is dimensionless and always larger than unity. In the limit $\ln \sigma \to 0$ the LNDF approaches the Gaussian distribution. The fraction of the particles with diameters in the range $x_i < x < x_{i+1}$ is given by

$$\exp\left(-\frac{(\ln x - \ln \bar{x})^2}{2 \ln^2 \sigma}\right) f_{LN}(x') d(\ln x').$$

The moments of the LNDF allow several useful relations for small particle statistics to be derived as shown in the Appendix.

**E. Comments on growth by absorption of atomic vapor**

Before the LNDF is compared with experimental data it is appropriate to comment on the neglect of growth by absorption of atomic vapor (cf. Sec. IV B).

If we for a moment assume that each atom on the surface of a growing crystallite in unit time can bind a certain constant number of atoms from the surrounding area, the growth of a spherical particle will be exponential,

$$\frac{dx}{dt} = kx,$$

where $k$ is the rate constant. Combined with a Gaussian distribution of times for growth (which might be argued for in the present context as due to a Brownian motion of the particles within the growth layer) we arrive at an LNDF for the diameters. This “derivation” of the LNDF was suggested by Kottler and by Irani; actually the idea goes back to an old work by Galton.

We do not believe such arguments to be applicable to inert-gas-evaporated particles, because if diffusion effects within the growth layer are considered, Eq. (13) can no longer be justified. An analytic treatment of growth by absorption involves the solution of a diffusion boundary-value problem with moving boundary conditions. In spite of its inherent mathematical intractability there are approximate solutions available, showing that initially $x \propto t$, and after a sufficient time $x \propto t^{1/2}$; these results are in clear contradiction to Eq. (13)! Consequently growth by absorption cannot easily account for inert-gas-evaporated particles.

**V. LOG-NORMAL DISTRIBUTION OF PARTICLE SIZES**

After some introductory remarks in Sec. VA, we discuss “log-probability” analysis of size distributions in Sec. VB, where we also present experimental data for particles with diameters $< 20$ nm showing that an LNDF is well obeyed. The log-probability analysis is of help in evaluation of oxide thicknesses for Al particles, as shown in Sec. VC, and is useful to see whether any minimum size exists for the particles, as discussed in Sec. VD. In Sec. VE we treat briefly the more complicated case of growth of large particles ($> 20$ nm) with well-defined crystal habit, where significant deviations from log-normality of the diameter distributions are found. Section V F discusses applications of the LNDF to ultrafine particles produced by exploding wires and by nozzle expansion, and Sec. VG summarizes all our data, as well as data from the literature, on $\sigma$ and $\bar{x}$ for particles produced by nucleation and growth in an inert gas.

**A. Introductory remarks**

The LNDF has been applied to finely divided matter

![Graph](https://example.com/graph.png)

**FIG. 9.** Number of particles counted per size interval versus diameter for the Al sample of Figs. 1 and 3. The dots represent midinterval values obtained from the size histogram. The curves show calculated frequency distributions for $x$ using $\Delta x = 1.05$ nm (cf. Fig. 1). The normalization is chosen such that the area under the curve is equal to 518, the total number of particles counted. Results for two different values of $\sigma$ are given. The arrow points to the location of the median diameter $\bar{x}$.
for a long time in such diverse areas as paint and rubber pigments, photographic emulsions, dust particles, crushed sand, aerosols for inhalation studies, cloud droplets, and exploding wire fragments. The particles for these studies have all been investigated by microscopy. Another application is to light-scattering data, where log-normal size distributions have been extracted from the experimental results for silver bromide sols, sulfur hydrosols, octanoic acid aerosols, and rutile pigments. As far as we know, however, the LNDF has not previously been compared with experimental size distributions for inert-gas-evaporation particles, in spite of the numerous articles published on this subject. Such a comparison will be the topic of this section.

We have already noted (cf. Fig. 1) that the experimental size distributions look skewed. This kind of asymmetry is precisely what one also obtains from the LNDF’s with $\ln x > 0$. Figure 9 shows a comparison between experimental data from the size distribution of Fig. 1 and the theoretical frequency distribution of $x$, as given by

$$\sum_i n_i f(L\ln x) f_{LN}(v),$$

where $L\Delta x$ is the magnitude of the size interval in the histogram and $f_{LN}(v)$ is defined in Eq. (9). The good over-all agreement is evident. However, a very accurate fit is difficult to achieve from the actual shape of the size distribution, and a better technique is to take recourse to graphical “log-probability” analysis as discussed and applied to many samples below.

B. Log-probability plots

It is straightforward to show from Eq. (9) that the fraction, $F_{LN}(v)$, of the total number of particles which have a diameter smaller than a certain size $x$ is given in terms of the error function by

$$F_{LN}(x) = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{\ln(x/\bar{x})}{(2\sigma^2/\ln^2)\ln 2} \right) \right].$$

This equation points directly towards the usefulness of logarithmic probability paper, on which $F_{LN}(v)$ versus $v$ yields a straight line. From such log-probability plots one can readily determine the constants $\bar{x}$ and $\sigma$ which characterize the LNDF. By its definition $\bar{x}$ is found at the $F_{LN}=50\%$ mark, and it can be shown that $\sigma$ is equal to the size corresponding to $F_{LN}=84.13\%$, divided by $\bar{x}$. From two points on the straight line it is thus possible to get both $\bar{x}$ and $\sigma$.

Figure 10(a) shows data for two of our Al samples. The circles, falling close to a straight line, represent the size distribution of Fig. 1. It should be noted that the cumulative percent has been plotted against the upper limit of the size histogram (rather than the mid-value as in Fig. 9); this is the only correct way of transforming the histogram into a probability plot. The circles and the open squares stem from two completely independent random samplings (as described in Sec. IIIA) of the particles, and the high reproducibility is proved. When particles were collected at the center of the cooling plate only, somewhat smaller sizes were found, as evidenced by the triangles. Thus the easy technique of sampling in one point is not reliable if very high precision in the size distribution is demanded. From the solid line of Fig. 10(a) one obtains 4.2 and 6.8 nm corresponding to 50 and 84.13%, respectively. Hence $\bar{x}=4.2$ nm and $\sigma=1.62$, which compares well with the “trial-and-error fit” of Fig. 9.

In Fig. 10(b) we present log-probability plots for two Sn samples. These represent different evaporations carried out with the same inert-gas pressure and oven temperature. Both samples were collected at the center of the cooling plate. Evidently, reproducible size distributions can be achieved by evaporating under identical conditions.

Figure 11 gives log-probability plots for some of our magnetic particles produced by conventional inert-gas evaporation from a filament. Once again it is seen that an LNDF is obeyed to a high accuracy. It is interesting to compare these results with size distributions by Kusaka et al. who investigated iron-based alloy particles produced in the same manner as ours. They reported “roughly Gaussian” distributions, but, as seen from Fig. 11(a), if their data are replotted on logarithmic probability paper, it becomes clear that the sizes...
are indeed distributed according to an LNDF to a high precision. The same is equally true for their published size distributions of Fe-Ni and Fe-Co-Ni particles.

For our largest Fe particles [No. 529B, cf. Fig. 11(a)] the experimental points tend to fall below the straight line for the smallest sizes. This deviation is statistically significant and represents a characteristic feature of particles with clear crystal habit as will be discussed in more detail in Sec. V E below.

C. Oxide thickness of Al particles

Log-probability plots for Al samples were reported in Fig. 10(a), where the results were based on dark-field microscopy. Figure 12(a) shows data obtained also with the bright-field technique. It is found that the bright-field sizes are larger, but that the points still fall close to a straight line, having a slope which is smaller than in the dark-field mode; hence the size distribution looks narrower when probed by bright-field microscopy.

These facts are easily explained by reference to the model for oxidized Al particles of Fig. 13. Here each particle is assumed to have an oxide coating which is at most weakly dependent on the diameter. As the amorphous oxide yields only diffuse scattering (cf. Sec. III B) which contributes insignificantly to the contrast in the dark-field mode, we can write the relation

$$x_{\text{bright field}} = x_{\text{dark field}} + 2t_{\text{oxide}}.$$  
(15)

If the vertical distance between the straight lines of Fig. 12 is set equal to $2t_{\text{oxide}}$ one can plot this quantity as a function of the cumulative percentage of particles smaller than a certain size. This is done in Fig. 12(b),

FIG. 12. (a) shows log-probability plots for Al No. 321 which was previously reported on in Fig. 10(a). The lower line is the same as the solid line in Fig. 10(a), and the upper straight line has been drawn to fit the bright-field data. The hatched area denotes the amount of oxide on the particles as discussed in the text. In (b) the vertical distance between the lines in (a) has been drawn with a linear ordinate. The fall off at the higher cumulative percentages is spurious as the straight lines in (a) clearly cannot intersect.

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If the vertical distance between the straight lines of Fig. 12 is set equal to $2t_{\text{oxide}}$ one can plot this quantity as a function of the cumulative percentage of particles smaller than a certain size. This is done in Fig. 12(b),
provided the inert-gas pressure is kept constant among months in ambient atmosphere at room temperature.

The Al oxide seems to be stable and does not grow noticeably during aging for out only a portion of those diffraction rings which in principle, limited to amorphous coatings. For crystalline oxides, however, one must be very careful to pick line oxides, however, one must be very careful to pick only on the amount of oxygen present during the evaporation, as noted in Sec. III B the color of these particles depends on $l_{\text{ext,de}}$, and with some experience one can get a fair estimate of the oxide thickness just by visual inspection provided the inert-gas pressure is kept constant among the different evaporations. The Al oxide seems to be stable and does not grow noticeably during aging for months in ambient atmosphere at room temperature.

The present technique to determine $l_{\text{ext,de}}$ for Al appears to depend only on the amount of oxygen present during the evaporation, such that $l_{\text{ext,de}}$ can easily be changed over a wide range just by admitting more or less O$_2$. As noted in Sec. III B the color of these particles depends on $l_{\text{ext,de}}$, and with some experience one can get a fair estimate of the oxide thickness just by visual inspection provided the inert-gas pressure is kept constant among the different evaporations. The Al oxide seems to be stable and does not grow noticeably during aging for months in ambient atmosphere at room temperature.

The present technique to determine $l_{\text{ext,de}}$ is not, in principle, limited to amorphous coatings. For crystalline oxides, however, one must be very careful to pick out only a portion of those diffraction rings which originate from the pure metal when looking in the dark-field mode. In practice this may turn out to be difficult.

D. Lower limit of particle sizes?

One can think of several reasons for the existence of a lower bound on the particle sizes. The most obvious, perhaps, is that the theory of homogeneous nucleation (cf. Sec. IV A) predicts a certain minimum size, $x_{\text{crit}}$, for an experimental smallest existing diameter, $x_{\text{min}}$, can be accounted for in an approximate fashion by changing Eq. (14), describing the cumulative fraction of particles smaller than $x$, to

$$F(x, x_{\text{min}}) = \frac{1}{2} \left( 1 + \text{erf} \left( \frac{\ln(x - x_{\text{min}})^2}{(2)^{1/2} \ln\sigma} \right) \right).$$

Figure 15 shows results of a calculation based on this equation for three different values of the ratio $(x_{\text{min}}/x)$. For $x_{\text{min}}=0$ one gets a straight line, as previously pointed out, whereas the other two lines display a positive curvature which becomes progressively larger as the ratio $x_{\text{min}}/x$ is increased.

No curvature in our log-probability plots for the smallest particles has been unambiguously established, and from this fact we estimate an upper limit for $x_{\text{min}}$ of 1 nm. This value might seem too generous, regarding the excellent fits to the straight lines in Figs. 10 and 11, but it should be remembered that the statistical significance is limited in the tail regions of the size distributions. Also results from dark-field microscopy are unreliable in giving a limit on $x_{\text{min}}$ for oxidized particles, because for an external diameter smaller than $2l_{\text{ext,de}}$ hardly any contrast is present. Therefore light-field microscopy has to be used, which yields a lower accuracy in the size determination.

An $x_{\text{min}}$ of 1 nm, say, is still much larger than the expected magnitude of $x_{\text{crit}}$. However, it demonstrates that the coalescence must start from very small particles.

E. Growth of large particles with crystal habit

In Figs. 9–11 it was seen that the distribution of particle sizes obeyed an LNDF to a high accuracy. This is no longer the case if one considers much larger diameters than those studied previously. Figure 16 shows results for large Zn and Mg particles and it is evident that an LNDF can account only for the main portion of the size distributions, whereas there appears to be an excess quantity of large Zn particles and of small Mg particles. The particles of Fig. 16 grow with pronounced crystal habit (cf. Fig. 4(b) and 4(c)), which makes an evaluation of the diameters more troublesome than for circular images, but this fact has been cor-

FIG. 14. Median diameter versus geometric standard deviation for those of our oxidized Al particles which have been carefully compared with an LNDF. Results are shown for different sampling techniques (one point or at random) and for different microscopic modes (dark field and bright field). Two specimens (No. 321 and No. 409) have been investigated both in dark field and bright field; their corresponding data points are joined by straight lines.

and it is found that $l_{\text{ext,de}}=1.0$ nm over most of the shown range; hence the assumption of a constant oxide thickness appears to be well founded.

The techniques of dark-field and bright-field microscopy have been applied to several samples of oxidized Al particles. Results for median size and geometric standard deviation are given in Fig. 14. Consistently

$$\bar{x}_{\text{bright field}} > \bar{x}_{\text{dark field}}$$

and

$$\sigma_{\text{bright field}} < \sigma_{\text{dark field}}$$
in agreement with the model of Fig. 12.

We have observed that $l_{\text{ext,de}}$ for Al appears to depend only on the amount of oxygen present during the evaporation, such that $l_{\text{ext,de}}$ can easily be changed over a wide range just by admitting more or less O$_2$. As noted in Sec. III B the color of these particles depends on $l_{\text{ext,de}}$, and with some experience one can get a fair estimate of the oxide thickness just by visual inspection provided the inert-gas pressure is kept constant among the different evaporations. The Al oxide seems to be stable and does not grow noticeably during aging for months in ambient atmosphere at room temperature.

The present technique to determine $l_{\text{ext,de}}$ is not, in principle, limited to amorphous coatings. For crystalline oxides, however, one must be very careful to pick out only a portion of those diffraction rings which originate from the pure metal when looking in the dark-field mode. In practice this may turn out to be difficult.

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$$F(x, x_{\text{min}}) = \frac{1}{2} \left( 1 + \text{erf} \left( \frac{\ln(x - x_{\text{min}})^2}{(2)^{1/2} \ln\sigma} \right) \right).$$

Figure 15 shows results of a calculation based on this equation for three different values of the ratio $(x_{\text{min}}/x)$. For $x_{\text{min}}=0$ one gets a straight line, as previously pointed out, whereas the other two lines display a positive curvature which becomes progressively larger as the ratio $x_{\text{min}}/x$ is increased.

No curvature in our log-probability plots for the smallest particles has been unambiguously established, and from this fact we estimate an upper limit for $x_{\text{min}}$ of 1 nm. This value might seem too generous, regarding the excellent fits to the straight lines in Figs. 10 and 11, but it should be remembered that the statistical significance is limited in the tail regions of the size distributions. Also results from dark-field microscopy are unreliable in giving a limit on $x_{\text{min}}$ for oxidized particles, because for an external diameter smaller than $2l_{\text{ext,de}}$ hardly any contrast is present. Therefore light-field microscopy has to be used, which yields a lower accuracy in the size determination.

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In Figs. 9–11 it was seen that the distribution of particle sizes obeyed an LNDF to a high accuracy. This is no longer the case if one considers much larger diameters than those studied previously. Figure 16 shows results for large Zn and Mg particles and it is evident that an LNDF can account only for the main portion of the size distributions, whereas there appears to be an excess quantity of large Zn particles and of small Mg particles. The particles of Fig. 16 grow with pronounced crystal habit (cf. Fig. 4(b) and 4(c)), which makes an evaluation of the diameters more troublesome than for circular images, but this fact has been cor-

FIG. 15. Log-probability plots calculated from Eq. (16) using $\sigma=1.50$, which is a characteristic value of the geometric standard deviation as seen from Fig. 14. Results are plotted for three different values of the ratio $(x_{\text{min}}/x)$. The lowest line is straight.
FIG. 16. Size distribution for large Zn and Mg particles with crystal habit. Both samples were produced by oven evaporation at $p(Ar) = 3.5$ Torr. The circles denote midinterval positions on the size histograms. The solid curves are calculated in the same manner as the ones in Fig. 9 using the shown values of median size and geometric standard deviation. The shaded regions indicate the "excess amount" of particles

rected for by approximating the cross-sectional area of the crystals with a circle and cannot be the sole reason for the discrepancy.

Figure 17(a) shows log-probability plots for some of our large particles of Mg, Al, and Zn. For all of these one notes a clear deviation from linearity near one of the ends (most commonly at the small-size end), which reflects the excess amounts of particles. The same general behavior is found if one extracts log-probability plots from the size distributions reported for Al particles by Yatsuya et al.\textsuperscript{37} as seen from Fig. 17(b).

The deviation from an LNDF is not due to the larger sizes per se, but appears to be correlated with the appearance of crystal habit. This point is illustrated by Fig. 18, showing a log-probability plot for large Ga particles growing as small droplets, i.e., totally in the absence of any crystal habit. Evidently the LNDF is fairly well obeyed. There are some uncertainties in the evaluation, though, because the smaller particles have a tendency to stick to the larger ones and hence become hidden on the pictures taken in the microscope. This effect probably accounts for the apparent deficiency of small particles (i.e., the positive curvature). The problem cannot be circumvented by going to dark-field

FIG. 17. (a) gives log-probability plots for our particles of Mg, Al, and Zn. Sample Al No. 004 was produced by filament evaporation at $p(Ar) = 15$ Torr together with a small quantity of $O_2$; the Mg and Zn samples have been reported on in Figs. 4(b), 4(c), and 16. (b) shows results derived from Fig. 13 of Ref. 37. Their data points have been taken to mean midinterval positions in a size histogram.

FIG. 18. Log-probability plot for the Ga particles depicted in Fig. 4(f).
microscopy as the particles are amorphous. In spite of this slight uncertainty we are convinced that an LNDF is in good agreement with the actual size distribution for sample Ga No. 1218. Thus any satisfactory explanation of the occurrence of "excess particles" must also explain its correlation with the appearance of crystal habit. One possible explanation is a rather trivial one: While the noncircular cross-sectional area of the particles was approximated by circles in obtaining the effective particle diameters, this may not be a proper procedure to follow. Indeed as it is the volume of the particles which is log-normal according to the theory of growth by coalescence (Sec. IV C), deviation from log-normal diameters can be expected as soon as crystal habit sets in or more precisely as soon as the volumes can no longer be expressed by Eq. (10). Empirically this usually occurs at \( x \approx 20 \) nm, and for diameter distributions with a significant number of particles both smaller and larger than this value there is almost constantly a "breaking point" in the log-probability plot at or somewhat above 20 nm [cf. Figs. 11(a), 17(a), 17(b), and 19]. Alternatively the presence of "excess particles" may be a result of a significant change in coalescence cross sections or kinetics which may occur once crystal habits develop. Clearly the point is far from resolved and requires additional study.

F. Particles produced by exploding wires or by nozzle expansion

Closely related to inert-gas evaporation are experiments where wires are exploded by current pulses in a noble-gas atmosphere to produce a small amount of ultrafine particles. Figure 19 shows a log-probability plot for Ag particles produced by the exploding wire technique; the results are reproduced from Ref. 86. Also included are results for Zn particles made by nozzle expansion using helium carrier gas. The data are replotted from the size distribution of Fig. 10 in Ref. 89 in the same manner as in Fig. 17(b).

G. Comparison of size distributions for inert-gas-evaporated particles

Figure 20 summarizes all the size distributions we have evaluated, including both our own results and data extracted from the literature. With very few exceptions the points fall nicely within a band given by

\[ \sigma = 1.48 \pm 0.12 \] 

inert-gas evaporation.

The only significant departure from this surprising rule is the result for Ga droplets that show a much wider distribution.

From the growth model of Sec. IV C, one might expect \( \sigma \) to increase with the number of coalescence events, i.e., with \( \bar{v} \); this is a consequence of the Central Limit Theorem. Obviously an evaluation of geometric standard deviation from measurements of diameters for particles with crystal habit contains a

\[ \sigma = 1.48 \pm 0.12 \] 

inert-gas evaporation.
GOLD SOLS

FIG. 21. Electron microscope images of colloidal Au particles produced by the Zsigmondy technique. Note the flocculent appearance of the particles in (b).

in this section we first treat particles produced by colloid chemical means (Sec. VI A). In Sec. VI B we discuss the applicability of our coalescence model of Sec. IV C to island structures in discontinuous films and argue that the islands ought to display an LNDF for the diameter distribution under rather general conditions. This supposition is verified by comparison with experimental results in Sec. VI C. Some comments on island growth by single-atom absorption are given in Sec. VI D. In Sec. VI E we turn to the related case of supported metal catalysts where also LNDF's can be applied successfully. Apart from some original experimental data on gold sols, the results given in this section are based on a compilation from the literature.

A. Colloids

Techniques to prepare colloids can be characterized as based on chemical vapor deposition rather than physical vapor deposition which we have considered till now. Here we show that LNDF's are found experimentally also for the former kind of particles.

We have investigated some gold sols prepared for this work by reduction of AuCl₄ with formaldehyde, according to the recipe by Zsigmondy. Figure 21(a) depicts annealed Au particles; they are found to be slightly oblong and well rounded. Many of the particles stick together in clusters. A log-probability plot for this sample is shown in Fig. 22, and clearly an LNDF is a good approximation for the size distribution. This observation is well corroborated by Au sols produced by the same technique by von Fragstein et al. Also included in Fig. 22 are results on mercury colloids (droplets); these data are reproduced from Whitehead. Evidently an LNDF is fairly well obeyed, even if statistically significant deviations can be observed. Results on Hg particles, being in good accord with those of Fig. 22, are reported also in Ref. 91.

FIG. 22. Log-probability plots for colloidal Au [cf. Fig. 21(a)] and Hg particles. The latter data were taken from Ref. 95.

FIG. 23. Median diameter versus geometric standard deviation for log-normal size distributions of particles produced by colloidal chemical techniques. The data points have the following designation: A, Ref. 94; B, Ref. 95 (cf. Fig. 23); C, Ref. 91.
In Fig. 23 we show median diameter versus geometric standard deviation for colloidal particles having size distributions that are well approximated by the LNDF. As for inert-gas-evaporated particles (cf. Fig. 20) the data for the crystalline colloidal particles form a band which is here defined by

\[ \sigma = 1.34 \pm 0.13 \]  

colloids;

it should be noted, though, that this result is based on rather few evaluations. The mercury droplets have significantly wider size distributions, just as Ga droplets had in the case of inert-gas-evaporated particles, which once more demonstrates that

\[ \sigma (\text{droplets}) \gg \sigma (\text{crystallites}) \]

For colloids the growth mechanism by single-atom absorption, described in Sec. IV E, is by no means excluded by the presence of an LNDF. In fact, it has been reported\(^7\) that the growth law for gold sols is exponential, as in Eq. (13). However, we believe that for our samples the growth proceeds predominantly by coalescence just as in the case of inert-gas-evaporated particles. This point is amply illustrated in Fig. 21(b), showing big Au grains which quite clearly consist of an agglomeration of smaller ones. Indeed dark-field microscopy revealed that these Au grains were composed of many smaller crystallites.

B. Applicability of the coalescence model to discontinuous metal films

As metal vapor is condensed onto a substrate the adsorbate goes through a number of distinguishable stages.\(^9\) The initial deposition leads to nucleation at many sites on the substrate; further deposition makes these nuclei grow mainly by absorption of single atoms arriving either by impingement or via surface diffusion (the latter mechanism is commonly phrased “Ostwald ripening”).\(^10\) By still further deposition, or by aging the nuclei structure, the film may enter a stage dominated by islands diffusing over the substrate surface to take part in collisions accompanied by liquidlike coalescence. Clearly this is a phenomenon with strong similarities to the growth of inert-gas-evaporated particles as discussed in Sec. IV C. Provided that only binary collisions have to be considered, and that the change of volume at each coalescence step may be assumed to be a random fraction of the volume after coalescence, the equations of Sec. IV C are valid also for the island structure of discontinuous films, which we have already pointed out in a preliminary note.\(^16\)

Some uncertainty, compared with the case of inert-gas-evaporated particles, enters because in the electron microscope only the diameter distribution (or fractional area distribution) for the islands on the substrate can be determined accurately. However, from Eq. (10) it is seen that an LNDF for the diameters is forecast for several different three-dimensional island shapes including spherical and half-spherical ones but not spherical caps. Log-normality is predicted also for rotation ellipsoids (symmetry axis perpendicular to substrate plane) with constant height, or for cylindrical islands of constant height. Because of this multitude of possible shapes that all give the same result within our theoretical model we believe the LNDF to be a good approximation of the diameter distribution of islands which can be observed in the microscope.

Most previous effects\(^98,99\) to treat coalescence theoretically have been centered around rate equations for atom cluster densities. This formulation, though, is rather awkward for determining size distributions, and no detailed predictions are available for the general case. Another approach was taken by Vincent,\(^100\) who studied the kinetics of island growth by a theoretical formulation put forward by Baroodyol and others\(^102-104\) to describe random coagulation phenomena. In Vincent’s work an asymptotic log-normal size distribution was used; however, this was introduced purely on ad hoc grounds, and furthermore no detailed comparison with experimental results was carried out.

C. Log-normal size distributions for islands in discontinuous films of Cu, Ag, and Au

This section gives a comparison between the LNDF and size distributions for islands in discontinuous films of the coinage metals (Cu, Ag, and Au). A similar treatment for supported metal catalysts is postponed to Sec. VIE.

A search through the vast literature on growth of discontinuous films turned up many published size distributions for island structures. Sometimes it may be difficult to judge whether, for a particular distribution, the island growth is dominated by liquidlike coalescence (as distinct from Ostwald ripening). An especially clear-cut example, though, is given by Skofronick and Phillips\(^105\) who studied gold films deposited on amorphous substrates of carbon or of silicon monoxide. They concluded\(^106\) that the island growth proceeded via binary collisions followed by coalescence of the colliding...
islands into larger ones, as required by our statistical model. Figure 24 reproduces one of their diameter distributions; it is seen to consist of a large number of very small islands in addition to a prominent peak centered at about \( x = 14 \) nm. The latter one, which is due to coalescence of the smallest islands, can be compared with an LNDF and, as also seen from Fig. 24, there is a very satisfactory agreement between the experimental data and the theoretical curve. This proves that, indeed, an LNDF is well obeyed. The agreement is demonstrated once more by the upper set of data points in the log-probability plots of Fig. 25. Good correspondence is found also for the other size histograms of Ref. 105, as exemplified by the lower data points of Fig. 25, as well as for size distributions reported by Faure et al.\(^{106}\) From the experimental conditions we believe that liquidlike coalescence is the significant growth mechanism for the experiments reported in these works. Generally, the agreement between theory and experiments is found to be best for the larger diameters which is understandable as accurate log-normality is predicted only when essentially all the particles have participated in many coalescence events.

In Fig. 26 we have plotted \( \bar{x} \) versus \( \sigma \) for several size distributions which have been taken from Refs. 105 and 107–109. Once again we find that all the data points fall in a narrow band which is here defined by

\[
\sigma = 1.28 \pm 0.06 \quad \text{island coalescence,}
\]

which implies that the size distributions under present consideration are significantly narrower than those for inert-gas-evaporated particles.

**D. Comments on size distributions of islands grown by single-atom transport**

The growth stage of discontinuous films where liquidlike coalescence dominates is generally preceded by another stage where single-atom transport is most important, as previously pointed out. For the latter kind of growth the LNDF has no theoretical justification;
be derived as in a work by Chakraverty,\textsuperscript{117} with subsequent emendations\textsuperscript{118,119} and extensions.\textsuperscript{220} Depending on whether the island growth is controlled by diffusion of monomers, or by an interface reaction, two somewhat differing shapes of the size distributions are predicted. In both cases the size distribution, $f_{\text{CN}}(x)$, is asymmetric but, in contrast to the LNDF, the tail is in the small-diameter side for both the limiting approximations mentioned above and on the larger-diameter side the distribution is identically zero above a certain well-defined size.

However, the differences become less apparent when the higher moments of the distributions are compared. Figure 27 shows the third moment of a theoretical diameter distribution for interface reaction governed growth. It is seen that over a fair portion of the curve it agrees well with the third moment of an LNDF ($\sigma = 1.078$). In an experiment measuring the properties of small particles it is often some higher-order moment that is most important, which makes the kind of comparison presented in Fig. 27 physically meaningful. Thus if one only pays attention to the larger diameters it should be possible to approximate the theoretical size distribution of particles grown by interface interaction with an LNDF for the purpose of comparing distribution widths. The same is equally true for island growth controlled by diffusion of monomers, provided one sets $\sigma = 1.04$.

Upon examining the available experimental data we have chosen to compare with the LNDF the experimental size distributions reported in Refs. 8 and 110–113, as we expect Ostwald ripening to be the dominant growth mechanism in these works. Generally an acceptable agreement is found; indeed, it is very seldom that the fit is as bad on the small-diameter side as one would expect from Fig. 27! Hence it is possible to extract unambiguous values for the geometric standard deviation. In Fig. 26 we have plotted $\bar{x}$ versus $\sigma$ and once again the data points for these approximate fits of the LNDF fall in a band, which is now determined by

$$\sigma = 1.16 \pm 0.05$$

Ostwald ripening.

The $\sigma$'s are thus somewhat larger than predicted from our fit with the Chakraverty-type theory, but significantly lower than for any kind of coalescence growth. For completeness it should be mentioned that size distributions for coinage metals are reported in Refs. 121–123 but for these works either the distribution is given only in a very coarse histogram, or the statistical significance is too bad to allow any definite conclusions to be drawn.

E. Supported catalysts

Supported catalysts are widely used in the chemical and automotive industries. They are discontinuous films of Pt, or some similar element or alloy, deposited onto an inert backing. From a technological point of view one of the most serious problems is high-temperature degradation by decrease of surface area\textsuperscript{118} (a similar degradation occurs for nonsupported catalysts\textsuperscript{224,225}). Evidently this is caused by island growth which makes a brief discussion in connection with Secs. \textit{E}–\textit{V}D worthwhile.

Size distributions for supported Pt particles are published in Refs. 126–132. For the great majority of the data an LNDF constitutes an excellent approximation, which clearly indicates that coalescence rather than Ostwald ripening is the most important growth factor. This is illustrated by Fig. 28 showing almost linear log-probability plots for Pt on NaCl\textsuperscript{126} and on alumina.\textsuperscript{127} Though it is not strictly speaking a catalyst, we have also included data for Co on alumina backing,\textsuperscript{133} because these discontinuous films were made by a catalytic preparation technique. Figure 29 provides a compilation of $\sigma$ as a function of $x$. The scatter among the points is larger than for the coinage metals given in Fig. 26 which might at least partly be caused by the
generally smaller size of the catalyst islands making microscopy more troublesome. Excepting the data of Ref. 129 an empirical relation
\[ \sigma = 1.32 \pm 0.12 \]
catalysts accounts for the data.

VII. SUMMARY AND CONCLUSIONS

The main new contributions of this paper are threefold:

(i) The development of a novel technique to make ultrafine metal particles;

(ii) the observation and explanation of a well-characterized shape of the size distributions;

(iii) the empirical finding that the distribution width is a function of the kind of technique used to prepare the particles (inert-gas evaporation, island growth in discontinuous films, etc.) rather than the detailed conditions for particle growth within each specific method.

The technique is a modification of the old inert-gas-evaporation method where, instead of having a resistive filament, the vapor is produced by well-controlled evaporation from a temperature-stabilized oven. By changing the evaporation parameters, particles of many different metals can be produced with median diameters within a wide range. With the new technique it was possible to produce well-characterized Al particle samples, weighing more than 1 g, with median diameters down to below 3 nm, and with the individual particles covered by an insulating oxide.

The particles nucleate and grow in a region above the surface of the hot metal. We have formulated a statistical model for this growth, based on the Central Limit Theorem, regarding only liquidlike coalescence of particles. The most salient prediction is that the logarithms of the particle volumes have a Gaussian distribution. Empirically we found that diameter distributions, as inferred from electron microscopy, agreed excellently with log-normal curves as long as the particles were too small to display crystal habit (in practice \(< 20 \text{ nm}\)), whereas for larger ones with well-defined crystal shapes significant departures occurred. These facts are consistent with essentially all size distributions for inert-gas-evaporated particles found in the literature and with our theoretical model.

For each of the techniques to make ultrafine particles we have discussed in this paper, we found that the geometric standard deviations fell within a rather narrow band. These surprising findings are summarized in Fig. 30. The narrowest distributions were found for discontinuous films in which the islands grow by Ostwald ripening. However, this observation is partly fortuitous because, as pointed out in Sec. VII D, the LNDF can be fitted only to the larger diameters. For islands growing by coalescence no such problems exist, and we found size distributions with still rather narrow widths. For supported catalysts the data were more scattered than for discontinuous coinage metal films, but the \( \sigma \)'s fell in similar ranges. All these size distributions were considerably narrower than for inert-gas-evaporated particles discussed in the main part of this paper. The results for Au colloids and for Ga and Hg droplets, as also given in Fig. 30, are founded on only a few measurements and are therefore somewhat uncertain. However there is no doubt that the liquid particles have by far the widest distributions.

It is important to note that the observation of the inert-gas-evaporated particles having wider distributions than for islands in discontinuous films does not necessarily imply that the former is an inferior fabrication technique, because it is much easier to obtain accurate size distributions by random samplings of the particles grown in a noble-gas atmosphere. For most experiments on the properties of ultrafine matter this fact ought to outweigh the advantage of a narrower (but less certain) size distribution of islands in discontinuous films.

ACKNOWLEDGMENTS

The authors wish to acknowledge their gratitude to Professor J. Silcox for his kind loan of the AEI electron microscope and to Professor M. Nelkin and Dr. M. S. Lu for helpful discussions concerning the statistical model of coalescence. They are also pleased to thank P. E. Batson and Dr. C. H. Chen for their expert assistance with the electron microscopy, P. E. Batson for kindly producing the Au sols, and especially C. M. Bastuscheck for producing some of the magnetic particles and for many useful conversations.

APPENDIX: MOMENTS OF THE LNDF

From the analytic form of the LNDF [Eq. (9)] it is straightforward to derive a relation of the 5th moment. The result is

\[ \sum n_i x_i (\sum n_i)^{1/2} = \exp(s \ln \bar{x} + \frac{1}{2} s^2 \ln \sigma), \]

(1)

from which the arithmetic mean diameter \( \bar{x} \), the diameter corresponding to average surface area \( S_{\text{ave}} \), or
average volume $\bar{x}_{m1}$ are obtained by

$$\bar{x}_{m1} = \exp (\ln x - ln\sigma),$$  \hspace{0.5cm} (A2)

and

$$\bar{x}_{area} = \exp (\ln x + ln\sigma),$$  \hspace{0.5cm} (A3)

Another useful relation connects the mode diameter [corresponding to the maximum value of $x^2 f_n(x)$] to the basic parameters of the distribution:

$$\bar{x}_{mode} = \exp (\ln x - ln\sigma).$$  \hspace{0.5cm} (A4)

For an LNDF with $\sigma = 1.5$, being a typical value for inert-gas-evaporated particles as seen in Sec. V.G, we obtain

$$\bar{x}_{m1}/\bar{x}^3 = 2.1$$

and

$$\bar{x}_{m1}/\bar{x}_{mode}^3 = 3.4.$$  

As an example we can apply these results to the mean splitting, $\delta_x$ of the energy levels of the condensation band due to quantum size effects. From the Kubo\textsuperscript{2} model we get $\delta_x (\bar{x}_{m1})^{3/2}$. If, erroneously, one uses $\bar{x}^3$ or $\bar{x}_{mode}^3$ as a measure of average volume, the predicted value of $\delta_x$ will be off with a factor exceeding 2! This demonstrates clearly the importance of an accurately known size distribution.

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*Supported by the National Science Foundation and the NSF-sponsored Material Science Center at Cornell.

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