# Lognormal Size Distributions in Particle Growth Processes without Coagulation

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A new model is proposed to explain lognormal particle size distributions found in vapor growth processes such as gas evaporation, without invoking coagulation. In the model, particles are moving by diffusion and drift through a finite growth region. The particle size is assumed to be a power function of growth time, and the final size distribution is determined by the first passage times. By computer simulation, lognormal size distributions and scaling laws interrelating the distribution parameters, the size of the growth region, and the drift speed were found. [S0031-9007(98)05606-3]

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The particle size distribution is a very important property of finely divided systems such as aerosols, emulsions, and powders. Particle growth processes and their influence on the size distribution have been studied for a long time and general theories exist [1–3]. In the case of growth from vapor, initial nucleation gives rise to droplets or particles which first grow by vapor absorption and then possibly by coagulation. A vapor growth process studied in great detail is the gas evaporation method for production of ultrafine particles with mean size in the nanometer range [4]. In this method, a metal is evaporated, and the vapor is subsequently cooled in an inert gas such as He. The technique was studied extensively by Granqvist and Buhrman [5]. Since then, intense development has taken place [6–8], and nanostructured materials composed of ultrafine particles have become important in fundamental and applied physics. In several such materials, extraordinary physical and chemical properties have been found [9–12]. Many of these properties depend critically on a small mean particle size and a narrow size distribution.

It was shown in [5] that the particle diameters $r$ after gas evaporation are well described by a lognormal distribution,

$$f(r) = \frac{1}{\sqrt{2\pi}\ln\sigma}\ \exp\left\{-\frac{(\ln r - \ln\rho)^2}{2(\ln\sigma)^2}\right\}, \qquad (1)$$

which is defined by the geometric mean diameter $\rho$ and the dimensionless geometric standard deviation $\sigma$. Also in [5], a coalescence model leading to lognormality was derived, and it was argued that growth by absorption of atomic vapor could not give rise to a lognormal particle size distribution. Subsequent work emphasizing the influence of absorption on the size distribution has been done [13,14], but lognormal distributions are usually explained by the Brownian coagulation models [15–18]. The applicability of these models can be questioned, since they are based on the theory of Smoluchowsky [1], which treats coagulation in a closed system of particles. A modern setup for gas evaporation is an open system, with particles constantly being added and removed. Furthermore, the coagulation models do not explain the origin of the lognormal distribution but rather assume its presence.

This Letter takes a different approach, which does not involve coagulation. A new model is proposed by emphasizing the time spent for growth, which has not been properly considered until now. It will be shown that the distribution of particle growth times can be accurately described by a lognormal distribution, and that growth by vapor absorption may indeed lead to a lognormal size distribution. This applies to any growth process where the basic mechanism is particle diffusion and drift through a finite growth region. Subsequent coagulation would not destroy the lognormality if the conditions are providing a self-preserving size distribution [18].

In modern gas evaporation equipment, an amount of metal is melted in a crucible in an evaporation chamber filled with inert gas. A steady flow of inert gas encloses the crucible. Ultrafine particles are formed in a growth zone above the melt and carried by the gas flow to a deposition chamber where they are collected. A one-dimensional model of this evaporation process was devised, in which the particles are formed and then transported by means of diffusion and drift through the growth zone, of finite length $L$. The drift is caused by the gas flow around the crucible as well as by a convection current in the gas that would be present even if no flow was applied. The particle size distribution is obtained by assuming that the particle size is a linear function of the growth time. To illustrate this assumption, consider growth of a spherical particle in atomic vapor. Atoms are absorbed by the particle, with surface area $A$, at a constant rate $\gamma$ per unit area and time. The particle volume $V$ increases according to $dV/dt = \gamma A$. Since $V \propto r^3$ and $A \propto r^2$, it follows that $r \propto t$. More sophisticated models yield the same result, or sometimes a different power-law dependence [19,20]. Note that the size distribution will be lognormal, if the time distribution is lognormal, for any power-law dependence of particle size on growth time. Finally, the model should also include a correction of the diffusion constant as predicted by the Einstein-Stokes formula. However, such a correction was not included since simulations indicated only a minor influence on the size distribution. These results will be published elsewhere.

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In the model, the distribution of growth times is the first passage time distribution of a one-dimensional random walk with a reflecting boundary at $x = 0$ and an absorbing boundary at $x = L$. In the simulations, an equivalent, symmetric problem was considered; see Fig. 1. A particle starts at $x_0 = 0$ and moves outward until one of the boundaries at $\pm L$ is reached. The random walk was implemented as

$$x_{t+1} = x_t + \epsilon_t + \delta s_t , \tag{2}$$

where the position at time $t + 1$ is given by the previous position, a random diffusion term $\epsilon_t$, uniformly distributed on $[-1, 1]$, and a drift term $\delta s_t$, where $\delta$ is the drift speed and $s_t = -1, 0, 1$ for $x_t < 0$, $x_t = 0$, $x_t > 0$, respectively. For each particle $i$, the number of time steps $t_i$ required to reach $\pm L$ was recorded. First passage time problems have been extensively studied [21,22], and a similar problem, with drift in the positive direction only and no boundary on the negative side, is known to have an analytic solution, the inverse Gaussian distribution [23,24].

Diffusion and drift are competing mechanisms of particle transport. The diffusion is described by a diffusion equation, $\langle x^2 \rangle = Dt$, where $D$ is a diffusion constant and $\langle x^2 \rangle$ is the mean-square displacement at time $t$. The mean is taken over an ensemble of particles. In the present model, $D = 1/3$. The mean passage time $\langle t_i \rangle$ then satisfies $L^2 = D\langle t_i \rangle$. The drift, with speed $\delta$, is described by an equation of motion, $x = \delta t$. A critical drift $\delta_0$ is defined for which the diffusion current and drift current are equal, that is, diffusion and drift yield the same mean passage times,

$$\delta_0 = \frac{D}{L} = \frac{1}{3L} . \tag{3}$$

Simulations were performed with different values of system size $L$ and drift $\delta$, and with at least $10^5$ particles to ensure good statistics. The RANLUX random number generator [25,26] was used for the simulations. The distribution parameters $\rho$ and $\sigma$ were estimated from the simulation data. Typical size distributions are shown in the log-probability plots of Fig. 2. In a log-probability plot, a lognormal distribution yields a straight line [5]. When the drift is small compared to the critical drift, $\delta/\delta_0 \ll 1$, the distribution is seen to deviate from lognormal; see Fig. 2(a). In an experimental situation, such a deviation from lognormality might still be too small to be observed. The large drift case, $\delta/\delta_0 \gg 1$, indicates lognormality to a very high precision. This is shown in Fig. 2(b). The tail points of the curves are not statistically accurate. In experiments, it is possible that the convection current alone is large enough to fulfil the condition $\delta/\delta_0 \gg 1$. It can be concluded that lognormal particle size distributions found in experiments can be explained in terms of growth time distributions. This holds in the case of gas evaporation as well as in other growth processes where particles diffuse and drift through a finite growth region. It should be noted that once initial nucleation has taken place, the proposed model fully accounts for the lognormal size distribution found in numerous experiments. Growth by vapor absorption is sufficient, and the model does not involve coagulation. However, if subsequent growth by Brownian coagulation would occur in regions where absorption cannot take place, this is known to be able to preserve the initial lognormal distribution [18].

In Fig. 3(a), the geometric mean particle size $\rho$ is normalized by division by $L^2$ and plotted versus normalized drift, $\delta/\delta_0$. The following scaling law is established:

$$\rho_s(\delta, L) = \frac{\rho(\delta/\delta_0)}{L^2} , \tag{4}$$

with $\rho_s$ denoting the scaled geometric mean particle size. In the small drift case, $\delta/\delta_0 \ll 1$, only diffusion plays a role, and the mean size does not vary with drift. When

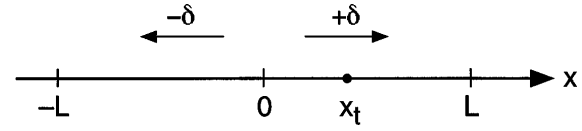


FIG. 1. The one-dimensional model used in the simulations. A particle starts at $x = 0$ and is transported by diffusion and drift, with speed $\pm\delta$, until it reaches $-L$ or $+L$.

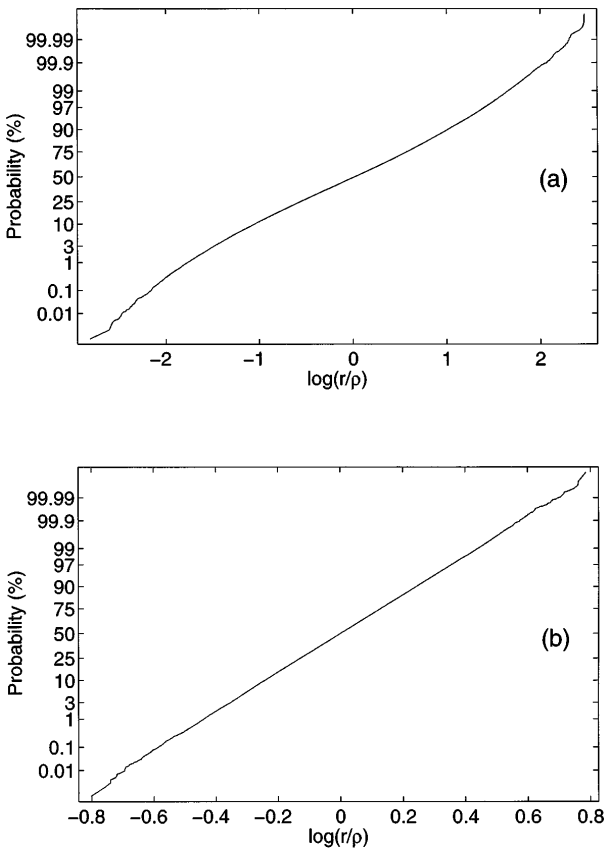


FIG. 2. Log-probability plots of simulated particle sizes. Number of particles $N = 10^5$, system size $L = 300$. (a) Small drift: $\delta/\delta_0 = 0.009$; $\rho = (2.006 \pm 0.01) \times 10^5$, $\sigma = 2.194 \pm 0.008$. (b) Large drift: $\delta/\delta_0 = 27$; $\rho = 9646 \pm 11$, $\sigma = 1.208 \pm 0.001$.

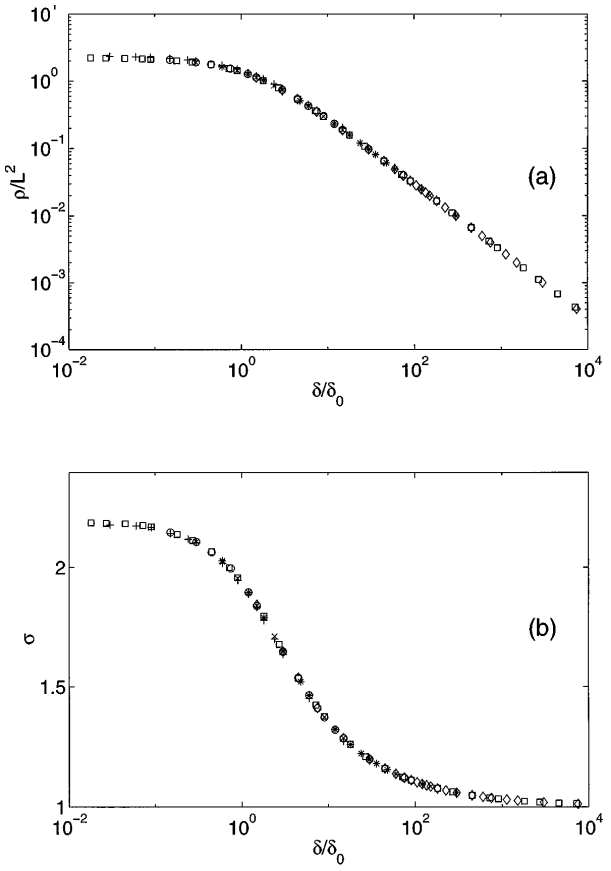


FIG. 3. (a) Normalized geometric mean particle size versus normalized drift. (b) Geometric standard deviation versus normalized drift. $+, L = 10$; $\bigcirc, L = 50$; $\times, L = 100$; $*, L = 200$; $\square, L = 300$; $\diamond, L = 500$.

$\delta/\delta_0 \gg 1$, diffusion can be neglected, and the normalized particle size is inversely proportional to normalized drift. Thus $\rho/L^2 \propto L^{-1}$ in this regime so that $\rho \propto L$, which is in agreement with experiments [27,28]. Figure 3(b) shows the geometric standard deviation versus normalized drift. This suggests a second scaling law for the scaled geometric standard deviation $\sigma_s$,

$$\sigma_s(\delta, L) = \sigma(\delta/\delta_0). \tag{5}$$

The geometric standard deviation is nearly constant in the small drift limit, $\delta/\delta_0 \ll 1$, and decreases when the drift increases. When the drift is very large, the geometric standard deviation approaches unity, which implies that the distribution tends to a Gaussian shape. It is seen that the influence of drift is strong on the geometric mean particle size as well as the geometric standard deviation. As mentioned, many applications of nanoparticles require both a small mean size and a narrow distribution, and the present results suggest that these conditions can be accomplished in practice by applying the largest possible drift, and by making the system size as small as possible. The scaling laws can be easily compared to experimental data. No such data appear to exist on gas evaporation, but the present work hopefully stimulates further investigation in this field.

To summarize, the distribution of growth times in particle growth processes similar to those underlying the gas evaporation method is proposed to give rise to lognormal particle size distributions. The model does not assume coagulation of particles; hence growth by vapor absorption would be the dominant growth mechanism.

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