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APPLICATION OF FRACTALS AND KINETIC EQUATIONS IN MODELING CLUSTER AND ULTRAFINE PARTICLE SIZE DISTRIBUTIONS

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Abstract — *We briefly describe a model which seems to be applicable to a variety of coalescence growth systems. Spanning cluster growth, particle growth and hillock formation in thin metal films, this model is based on the Smoluchowski kinetic equations and fractals. We describe how this model has been able to suggest the effect of translational to internal energy conversion in coalescing systems in determining the shape of particle size distributions. We also suggest how this model can be employed to account for the behavior of hillocks in supersaturated alloy films under thermal annealing conditions.*

INTRODUCTION

One of the more enticing materials science oriented applications of laser chemistry is the synthesis of cluster and ultrafine particles using organometallic precursors (1). Clusters and ultrafine particles are predicted (2,3) to have a variety of unique electrical and optical properties, which allow revealing investigations of the scaling of fundamental properties and could also allow important applications. Models (4,5) exist that connect the distribution of cluster sizes present in a bulk sample, and the microscopic properties of the cluster, to the electrical, mechanical and optical properties of the bulk material. A model (6) is needed to connect a particular distribution produced to the particular set of reaction conditions used to synthesize those clusters. Although numerical treatments (7,8) have been in existence for some years, we seek an analytic model which may be of intuitive value in addition to empirical value. The problem is complex because of the importance of multiple kinetic pathways in the synthesis of any cluster containing more than a few monomers. We report progress in exploring the utility of a model based on the Smoluchowski equations. As an illustration of its potential generality, we also mention recent progress in exploring the applicability of the same model to hillock formation and growth in thin metal films.

The model is presented in detail elsewhere (9) so only the general concepts will be described here. The basic idea is contained in the Smoluchowski equations [1] which were introduced (10) in the context of colloidal aggregation and solved in the limit of cluster/particle growth in

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{j=1}^{k-1} K_{j,k-j} n_j n_{k-j} - n_k \sum_{j=1}^{\infty} K_{j,k} n_j \quad [1]$$

chemical solutions in 1916. Here, n_k is the number density of clusters containing k atoms. Only binary collisions are considered and reaction rates are calculated as collision frequencies using number densities and cross sections, or in the particular language of fractal coalescence studies, number densities and “kernels”. These kernels have the form of second order rate constants which, multiplied on number densities of the different cluster sizes, give the net rate of formation of the clusters. A given cluster size is formed only by the coalescence of smaller clusters and is destroyed only by its coalescence with other clusters to form still larger ones. This is a mean-field type treatment in that no spatial correlation is presumed to exist between different cluster sizes.

The information mediating the various interactions involved in aggregation chemistry is contained in these kernels. There are essentially three analytical approaches which have been applied to cluster and particle formation. Each leads to a theory which relies on basic input parameters taken from one limit in the problem. Using a thermodynamic approach (*e.g.* the Kelvin equation) (11) and employing homogeneous nucleation theory (12), in which aggregation occurs by addition of monomers, one bases the parameters of the model on the energetics of bulk materials.

Alternatively, one can begin in the opposite limit and attempt to approach understanding the kernels based on the properties of the individual monomers (8,13,14), which are calculated and extrapolated using quantum chemical calculations. The third approach, our approach, is to focus on the scaling of the properties of the clusters and particles and the reacting system from the microscopic regime to the bulk regime.

To illustrate the physical content of scaling, we refer to the following example. In some agglomerating systems, the so-called “ballistic” regime, the clusters’ mean free paths are long compared to their own size. As the number of monomers in a cluster is increased, the cluster’s size increases. In our model of this case, the probability per unit time that a particular cluster will interact with, and agglomerate with, another cluster increases with size because the amount of space explored per unit time increases with increasing size. However, for a constant temperature system, the more monomers in a cluster, the greater its mass and the slower it moves, thereby exploring less space per unit time in the reaction medium for coalescence partners. An identical situation can be shown for systems evolving with diffusion limited mass transport.

Do the rate constants, *i.e.* kernels, increase or decrease with increasing sizes due to the competing tendencies? Which tendency prevails in a particular agglomerating system depends on the shape, represented in terms of the fractal dimension, of the growing particles. A particle can grow in various ways such that its average cross-sectional area increases in correspondingly different ways. Which tendency prevails also depends on how quickly the clusters slow down with increasing size. Exothermicity or endothermicity of agglomeration, evaporation effects, as well as the efficiency of conversion of center of mass translational energy and angular momentum into internal energy and angular momentum can affect the distribution of velocities and thereby mass transfer rates. Thus, the *scaling* of the kernels with increasing cluster size, *i.e.* number of monomers in the cluster, is the issue in our model. The actual values of the kernels (15) are important for connecting a particular simulation or analytic result based on [1] to a particular set of reaction conditions. Rigorous calculations in the ballistic or diffusion-limited mass transfer regime suggest that the scaling of kernels should be represented as [2].

$$K_{\lambda_i, \lambda_j} = \lambda^{2\omega} K_{ij} \quad [2]$$

There is an implicit assumption in the literature that the scaling varies smoothly as reaction conditions are changed from the ballistic to the diffusive regimes. Using [3], which is equivalent to [2], absolute values for all kernels can be calculated within a single constant multiplicative factor from the number of monomers in each of the interacting clusters and the scaling parameter, ω . We have already described (15) how to obtain this constant factor from appropriate experimental measurements.

$$K_{i,j} = K_{1,1}(ij)^\omega \quad [3]$$

When (2) is obeyed, the kernels are said to be homogeneous. For homogeneous kernels, Jullien (16) found an asymptotic solution for the Smoluchowski equations, [4]. Here, $a = -2\omega$ and b depends on t .

$$n_k \rightarrow A k^a e^{-bk} \quad [4]$$

Jullien's solution [4] and the well-known lognormal distribution function are very similar. Using a Taylor's series expansion of [4] about the most probable cluster size, it is possible to show (9) that [4] and the lognormal distribution are nearly identical. The lognormal distribution has long been associated with coalescence growth (6), but the only mathematical justification has involved random numbers and the Central Limit Theorem.

There have been many empirical uses of the lognormal distribution over the last century and a half (17), including particle size distributions relating to objects created by breaking down larger objects. For this, the Rosin-Rammler probability density distribution function (18) has also been used extensively. Both of these distributions can be seen to resemble Jullien's rigorous solution to the Smoluchowski equations. In the case of breaking-down phenomena producing particle size, *i.e.* fragment size, distributions, we suggest that coalescence growth is again the ultimate cause. In this case we suggest that a substantial portion of the net breakdown process occurs at grain boundaries. These boundaries are mostly determined by the process mediating the growth of the grains.

Determination of the ω corresponding to a particular set of cluster or particle size data can be accomplished in a variety of ways. For experiments involving mass spectrometric determination of cluster size distributions or others for which a set of non-zero populations exist, equation [5] is advantageous. A plot of $\ln(n_k)$ can be fit to a bilinear form in k and $\ln k$, and thereby yield a and b directly. Data from other sources is often represented using "bins" to produce histograms.

$$\ln(n_k) = \ln A + a \ln k - bk \quad [5]$$

When some of the bins contain zero observations of a given cluster size or size range, fitting the cumulative distribution is advantageous. This can be fit to also give a and b directly which is tantamount to knowledge of ω . Earlier (9), we employed the lognormal distribution to estimate the average cluster size, $\langle k \rangle$, and the most probable cluster size, k_m , for a particular set of data. Given these values and [6] we calculated ω .

$$\frac{\langle k \rangle}{k_m} = \frac{a+1}{b} = \frac{2\omega-1}{2\omega} \quad [6]$$

We have calculated and compared values of ω from a set of nozzle beam expansion-produced cluster size distributions. We have since recalculated ω values from these data, which are somewhat different from those earlier published values (9). Since the value of ω depends on reaction conditions in addition to the nature of the monomer, comparability across various experiments is not immediately assured. It was observed, however, that its value is usually more negative than anticipated by the theory. Simulations show that significant loss of all coalescing species from the reacting system, *e.g.* by diffusion out of the reacting volume, leads to size distributions having more negative values of ω . In particular, for the apparent value of ω to be affected, the loss rate must decrease with increasing mass. As will be discussed further below, this general observation may suggest that all clusters slow down faster with increasing cluster size than predicted, based on the kinematics of the conversion of center of mass translational energy to internal energy. Based on this idea it was possible to rationalize the values of ω obtained, based on the position of the monomer in the periodic table.

Simulations (9,22) based on integrating [1] suggest that the value of ω obtained from a particular size distribution is not affected if only a subset of kernels is arbitrarily changed from the homogeneous values. This case is important because consideration of the properties of clusters based on the properties of the constituent monomers inevitably suggests that when certain numbers of monomers are involved, special structures can be formed. Sometimes a structure is thought to be special because the cluster, a "magic number cluster", is coordinately saturated, *i.e.* there are no places that even one additional monomer can attach without first breaking other bonds in the cluster. C_{60} is such a magic number cluster. Other times the number of monomers leads to a so-called "shell closing" involving the number of valence electrons associated with the whole cluster, much as shell closings are the underlying basis for the ordering of the elements in the periodic table. Such shell closings (13) are thought to be evident in the cluster size distributions of many elemental monomers, *e.g.* sodium was an early prime example. The existence of a "magic number" cluster would seem to affect only a subset of the total set of kernels, whereas evaporation or diffusion could directly affect the populations of *all* cluster sizes. When all sizes are affected, the perturbation is "global" and a different ω is manifest. Based on the ability of a homogeneous set of kernels to represent actual data and the existence of multiple kinetic pathways for producing any cluster with more than a few monomers, all clusters which are not magic number clusters probably exist in a range of different structures that for the purposes of kinetics are indistinguishable. Magic number clusters are the only ones with unique structures and, in all likelihood, have coalescence kernels which are smaller than that predicted by homogeneity.

Our interest in the lognormal distribution originated in its apparent applicability to modeling certain aspects of thin film morphology. Depending on deposition conditions, *e.g.* substrate temperature and deposition rate, metal films can be deposited which possess structures known as "hillocks" because of their appearance in electron micrographs (19). Backscattered and secondary electron studies at variable angles of incidence can be used to study these objects and determine their morphology and locations in the films. It is thought that material at grain boundaries moves under the influence of compressive strain and participates in some type of coalescence growth. This leads to a temporal variation in the distribution of hillock sizes.

We have attempted to apply our coalescence model to the formation and growth of hillocks using the published data of Vook (20) and coworkers. Although this particular study involved hillock chemistry stimulated by thermal annealing, we hope to extend this approach to electromigration (21) induced hillock chemistry. The system studied involved passivated, ≈ 1000 Å thick films of evaporated aluminum-copper alloy, 15 at. wt.% copper in aluminum, on native oxide coated silicon.

Although this study will be described in detail in a separate publication (22), certain conclusions are forthcoming. One test of the model is to show that Jullien's solution is better than other functional forms in representing the data for pure metal. In fact, no other form is better at representing it although very similar forms, *e.g.* the lognormal distribution, represent the data equally well. The data for one alloy film is slightly better represented using the lognormal distribution although it should be noted that our model is applicable only to pure clusters, particles or hillocks. Another aspect of the model involves the time evolution of the b parameter. While it is expected that b should vary in time so as to be proportional to $t^{1/(2\omega-1)}$, a is expected to be time independent. Application to Vook's data gives a value of ω , based on the value of a , that does vary in time. Notwithstanding this discrepancy, if one uses the average value of ω obtained over the time series, it is true that the b parameter varies more or less as expected.

This case is particularly interesting because we have reason to believe that the value of b obtained from experimental distributions will be more reliably determined than the value of a . Thus, the value of $\omega = -0.25$ obtained from the time dependence of b may be worthy of more interpretation. The scaling parameter ω can be expressed using equation 7 in terms of: (i) the scaling of velocities with cluster number α , (ii) D , the fractal dimension of the clusters/hillocks, (iii) d_w , the fractal dimension of the agglomerating species' trajectories, and (iv) d , the dimensionality of the space in which the coalescence growth is occurring.

$$2\omega = \alpha + (d-d_w)/D \quad [7]$$

Equation 7 is obtained (9,16) by requiring the kernels we have been using to describe the kinetics to behave in such way with changes in space and/or time scale such that overall solutions of the Smoluchowski equations are invariant to such scale changes. This is thought to be required because clusters, and the size distributions associated with a population of them, are thought to be "self-similar." This is to say that a distribution of clusters has special properties with regard to comparing the structures of large and small clusters with each other. Based on the idea that films are not terribly far from thermal equilibrium, it seems plausible that hillocks and clusters would have velocities distributed as a Maxwell-Boltzmann distribution. If this is true, then the average velocity of the distribution should vary as the inverse square root of the mass and we expect α to have a value of -0.5 . Since α is the only negative contribution to ω , it is clear that if experimental data yields $2\omega < -0.5$, such as obtains in gas phase clustering experiments, then there is some other process occurring which causes clusters to slow down. Note that the coalescence of clusters in gas phase coalescence growth involves the conversion of center of mass translational energy of coalescing clusters into internal motions, *i.e.* rotations and vibrations. This maintains constant temperature. So the slowing down we are considering is in excess of this effect and must somehow involve the buffer gas or some other dissipative interaction such as emission of radiation.

As mentioned above, simulations have shown that if there is a loss of material by diffusion, the apparent value of ω is in fact decreased. In the case of the hillock data, this loss of material

does not seem to play an important role. The temperatures used and the conditions of observation make loss by vapor transport unlikely, although the loss of aluminum by precipitation with copper may have had some effect. The value of ω obtained suggested that $(d-d_w)/D \approx .25$. Since $d_w \approx 2$ in a condensed phase and $3 < D < 2$ seems plausible based on the appearance of the SEM data, we deduce that $3 < d < 2$. Thus, the motion of the hillocks responsible for the coalescence growth probably occurs in a space having fractal geometry. This suggests that the regions bounded by grain boundaries should not be thought of as surfaces or as fully three-dimensional volumes.

We are encouraged by these observations in so far as the experiment was not designed to isolate the types of comparisons we have attempted. The particular alloy being used for the time evolution experiment was supersaturated in one component with respect to another so that a precipitate was being formed which could affect the value of ω . The experiment was not able to clearly observe the smallest objects contributing to hillock growth and Vook pointed out that these smallest entities were important. Observations on the largest spatial scales are also limited. Given these potential sources of experimental artifacts and competing physical processes not contained in the Smoluchowski treatment, it seems remarkable that the model discovers any order in the data at all. This study suggests that a study can be designed which could unequivocally discern whether the model is uniquely suited to modeling hillock formation and growth. As a practical matter, the model already suggests that the interpretation of the effect of background gases on the formation of hillocks during deposition needs to be reexamined.

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