Distribution Kinetics--A New Approach to Cluster Dynamics and Self-Assembly

Assembly of molecules (monomers) into clusters and then into ordered structures is ubiquitous in nature and also offers exciting opportunities to synthesize new and useful products. We propose to build on our work that applies distribution kinetics to macromolecular interactions and chemical mechanisms by developing a new distribution kinetics approach to cluster kinetics and dynamics. The goal is to describe quantitatively the spatial and temporal evolution of cluster size distributions. Our recent publications already show accomplishments and hold significant potential for a comprehensive theory of *nanostructure kinetics and dynamics*. The XYZ* group has laid the groundwork for understanding nucleation, particle growth and dissolution, ripening, phase transitions, and aggregation/deaggregation by a unified theory. We propose to explore, both theoretically and experimentally, how *distribution kinetics* can provide insight into combining these processes that underlie the complex phenomena of self-assembly. We also propose experiments that will substantiate the theoretical predictions in our current publications and those that will arise out of the proposed work. The subject is of intense fundamental as well as practical interest, and warrants the increasing attention of researchers with different backgrounds.

The proposed work hypothesizes that a model based on a new reversible population balance equation provides a consistent and general approach to cluster processes such as nucleation, crystal growth and dissolution, ripening, phase transitions, and aggregation/deaggregation. The model breaks with tradition by following macromolecular (polymerization-depolymerization) kinetics to simulate reversible random fission-fusion and reversible monomer addition-dissolution processes. In addition to reversibility, the model has several attributes that other theories may not have, including evolution to equilibrium or steady state for closed batch or open flow systems, respectively. The cluster-size distribution (CSD) is the key dependent variable at the heart of the theory. The CSD spatio-temporal dynamics are mathematically described by means of population balance equations representing all the nucleation, growth and dissolution, ripening, and aggregation/deaggregation processes and interacting constituents. In our research group we solve the population balances mainly by moment methods, which may entail similarity mathematics leading to spatial fractal or temporal self-similar behavior. The approach is consistent with less-detailed thermodynamic and irreversible population balance approaches and makes contact with experimental observations through mass moments of the particle-size distribution.

The theory may reveal new possibilities or perhaps limitations on self-assembly methods of nanotechnology. For example, we describe how Ostwald or random ripening can frustrate attempts to manufacture nanocrystals. As with all chemical manufacturing methods, a reliable and comprehensible theory is essential to guide planning, design, implementation, and operating stages.

The example of cluster growth, dissolution, and ripening illustrates the outlines of the theory. We show that reversible monomer addition to clusters intrinsically produces dispersed cluster growth--no arbitrary, *ad hoc* procedures to introduce growth dispersion are needed. Growth dispersion yields size distributions that evolve from nuclei of uniform size. Rate coefficients for monomer addition or its reverse are considered to depend on cluster mass as a power expression, x^{λ}. Analytical calculations of moments are possible for $\lambda = 0$ and 1, which can be interpreted to represent, respectively, diffusion-limited and surface-controlled growth regimes. These two cases represent extremes of size-independent and size-dependent growth, yet yield similar results. The implicit growth dispersion, leading to a polydisperse cluster-size distribution, is a significant virtue of the current theory. The CSD evolves to equilibrium for a batch and to steady-state for a stirred flow system. The first three moments provide the number, average mass, and CSD variance, which allow representation of the CSD by two-parameter, normalized statistical distributions, such as lognormal or gamma distributions. With realistic initial conditions, operating parameters, and rate coefficients, the new theory describes typical crystal growth and recrystallization processes, including Ostwald and random ripening. The algebraic moment expressions are readily evaluated, and agree with general features of observed crystal growth behavior.

* The name of the group was changed to XYZ for customer information protection.