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Comment

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Comment on "Fitting and Interpreting Transition-Metal Nanocluster Formation and Other Sigmoidal-Appearing Kinetic Data: A More Thorough Testing of Dispersive Kinetic vs Chemical-Mechanism-Based Equations and Treatments for 4-Step Type Kinetic Data"

It should come as no surprise that the 4-step F−W model, containing four empirical fit parameters,[1] fits the data more precisely (i.e., with higher R^2 values) than my two-parameter kinetic models and the two-parameter Avrami equation. While a direct comparison of the raw AICc values (from eq 5), as opposed to the *w* and ER values provided in Tables 2 and 3, *might be* more meaningful (and less suggestive of hyperbole[2])—vide infra—it is highlighted here that there exist significant issues with the use of the 4-step F−W model that remain to be addressed.

Two points are important here: (1) by considering the dispersive nature of nanoparticle/cluster formation, it might be possible to derive a simpler equation that fits the data comparably to the 4-step model and (2) determining the best kinetic model for a particular application does not reside solely with a comparison of the empirical curve fits of the various models (as the authors have done, using an AIC-type approach), but also with a comparison of the physical interpretation and meaningfulness of the fit parameters extracted from the data, taking into account their associated errors. From the previous Finke literature, it is clear that the 4-step model has shortcomings with respect to point 2, likely because it fails to acknowledge point 1.

The $10^{\pm 4}$ uncertainty associated with the "nucleation rate constant" in the 4-step F−W model[3] is, simply put, unacceptable (note the absence of fit parameters/associated errors for the 4-step F−W model in the title paper). Curve fit preciseness becomes irrelevant in cases where the apparent rate constants extracted from the data have such large errors associated with them so as to render them unusable for interpretation/further analysis. That issue is often encountered in cases of overfitting the data, a point suggestive of the fact that the 4-step F−W model might be overparameterized (although that issue was not detected by the authors' treatment).

Nucleation-and-growth is largely considered to be a single mechanism in the solid-state kinetics literature, dating back to the original derivations of the "Avrami" model. Note that this mechanism might also be applicable to nanoparticle/cluster formation (producing sigmoidal/"sigmoidal-like" conversion transients), as such conversions, too, involve a phase transformation (dissolved monomers to nanosolids) that occurs via critical nuclei. However, in the latter case, as opposed to most crystallizations, the (faster, thus, not rate-limiting) growth step is typically *surpressed.* Unlike the 4-step F−W model, the Avrami model does not relate a series of elementary processes whereby the nucleation−growth−agglomeration steps can be readily decoupled. In fact, it is difficult to conceive (i.e., it is improbable) that there could exist four such distinct "reaction steps", all of which have such remarkably similar activation energies that they must be considered simultaneously (together) to adequately describe the sigmoidal kinetics pertaining to the *rate-limiting step* of the nanoparticle/cluster formation. Especially so, given the fact that some of those rate constants (assuming a fixed pre-exponential factor, as per the Eyring equation) often differ from each other by *five or more orders of magnitude*.[3,4] Granted, the autocatalytic and first-order rate constants have different units, which can complicate their direct comparison, but then what is the physical significance of molarity (from the "reporter reaction") in describing the formation rates of solids? Nanoparticles/clusters ultimately form colloidal suspensions, *not solutions*.

In sharp contrast to the 4-step F−W equation, my current dispersive kinetic models contain only two empirical fit parameters, keeping with the "Ockham′s razor" philosophy (note that their physical interpretations have been provided elsewhere[5]). Each model is based on a simple, first-order conversion mechanism; in that sense, they are no less "mechanistic" in nature than the F−W models, but they are simpler and, thus, more probable. Overfitting has not been a problem with these models, based on my experience.

Fundamentally, chemical kinetics approaches useful for treating reactions in homogeneous solutions are unlikely to be appropriate for describing nanoparticle/cluster formation in many dispersions, for much the same reason they are not useful for modeling certain solid-state kinetics (i.e., processes that are nucleation/denucleation rate-limited). Such processes are more likely to involve a simpler rate-limiting mechanism (e.g., a single step), but one that necessitates the use of a distribution (i.e., "large number") of rate constants due to the different activation energies experienced by the monomers during the course of the conversion (resulting from continuously renewing

(1) Finney, E. E.; Finke, R. G. *Chem. Mater.* **2009**, *21*, 4468.
(2) Regardless of the "highly nonlinear" behavior of the *w* function, the fact that a model producing an R^2 value only 0.0022 lower than another model, but using only half the number of fit parameters, has an "evidence ratio, ER", (and, hence, an inferred relative probability of being accurate) of only 10^{-32} seems unreasonable. Holistically, calculated values smaller than Planck's constant (*w*) or as large as 10^{211} (ER) should likely be flagged in the chemical literature because their meaningfulness is lost due to the sheer magnitudes of the numbers.
(3) Finney, E. E.; Finke, R. G. *J. Colloid Interface Sci.* **2008**, *317*, 351.
(4) Finney, E. E.; Finke, R. G. *Chem. Mater.* **2008**, *20*, 1956.
(5) Skrdla, P. J. *J. Phys. Chem. A* **2009**, *113*, 9329.

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environments). That concept is central to dispersive kinetics. While the authors called dispersive kinetics a "nontraditional subarea of chemical kinetics", it is noted here that Plonka[6] used such an approach to obtain the general form of the Avrami equation (originally derived ~70 years ago using crystal physics), which has remained a cornerstone in the modeling of nucleation rate-limited kinetics to this day.

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(6) Plonka, A. *Annu. Rep. Prog. Chem. Sect. C* **1988**, *85*, 47.