Methods for the Prediction of Nanoparticle Fate and Transport in an Aqueous Environment

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ABSTRACT

The development and applications of nanomaterials have presented a unique problem to environmental scientists and risk assessors. Until now, the models and paradigms used to predict the behavior of chemicals in the environment and thereby the potential for exposure and effect have been firmly rooted in the principals of solution chemistry such as molarity, partition, fugacity, etc. However, to evaluate and predict the behavior of nanomaterials in the environment, new considerations that take into account conditions of surface chemistry need to be added to the standard model. These include environmental and material properties such as buoyancy, surface area, viscosity, charge accumulation, steric factors, and Hakman forces. Recently, we presented a method for predicting the mass transport and stability of nanomaterials in the environment using competitive probability kinetics. Furthering on this research, this work looks at predictive methods of determining the probability of reaction (P) given projected rates of interaction. This is placed in the context of likely modes of receptor exposure. With consideration of bioavailability and toxicological potency and efficacy, this will permit the direct risk evaluation of potential environmental impacts within the paradigm currently in use.

Keywords: Nanoparticles, Solution, Thermodynamics, Modeling, Fullerene

1 INTRODUCTION

A compound is a nanomaterial not by virtue of its composition, but rather by virtue of its size. Nanoparticles are considered to be any insoluble entity with one or more dimensions of less than 100 nm. The size of the particle affects the properties of the material in three dramatic ways. First, smaller nanoparticles, particularly those less than 50 nm in diameter, cease being governed by classical physics, and become more subject to the laws of quantum physics. Second, the reduction in particle size dramatically increases the surface area to mass ratio such that the surface properties become predominant [1]. Third, the reduction in particulate mass affects the classical physics of the particles such that materials that usually do not form homogeneous solutions in liquids or gasses are able to form heterogeneous, metastable suspensions. This allows materials that previously were excluded from environments by virtue of their phase properties to now exist in them.

Previously, it was demonstrated that chain reactions between nanoparticles in suspension could be predicted using stochastic probability in collision kinetics [2]. While collision kinetics can predict rates of physical interaction, determining the actual reaction rates is challenging because it requires the prediction of the probability that a collision will result in an irreversible combination. Nanomaterials depart from classical chemical thermodynamics because the size of the particle impacts an aspect of kinetic energy that usually can be disregarded in predicting an interactions activation energy and overall free energy.

In this current work, statistical thermodynamics is applied to the previous collision model in order to better characterize and predict the potential interactions of nanoparticles in the environment.

2 THEORY

2.1 Estimation of emulsion stability

Metastability is the state where a suspension is able to behave like a solution by virtue of the particles' individual densities relative to their settling rates. The apparent solubility (k_{as}) of a nanoparticle in an aqueous medium can be described as a function of the buoyancy of the nanoparticles and can be expressed using Boltzman's equation as follows:

$$\ln k_{as} = \ln \frac{[X]_{aq}}{[X]_S} = -\frac{Vgh(\rho_X - \rho_{aq})}{kT}$$

Where g is the gravitational constant, k is Boltzman's constant, T is the absolute temperature, V is the particle volume, and ρ_X and ρ_{aq} represents the density of the nanomaterial and the aqueous medium, respectively. Since the amount in suspension will have no real affect on the amount not in suspension, it is possible to determine the total equilibrium suspended particulate concentrations from the integration of the Boltzman's equation to derive an expression that can be used to describe the concentration as follows:

$$[X]_{aq} = [X]_0\, e^{-\frac{Vg(\rho_X - \rho_{aq})}{2kT}\cdot \Delta h^2}$$

If the nanoparticles have an affinity either for themselves or other constituents in the environment, then the metastability described above will be altered over time based on the interactions between these species. For a binary reaction, the initial rate constant for constituents X and Y (k'_{XY}) is defined as follows:

$$k'_{XY} = P_{XY}\,\frac{2kT}{3\eta}\cdot\left(2 + \frac{r_X}{r_Y} + \frac{r_Y}{r_X}\right)$$

where P_{XY} is the probability of a reaction given an interaction.

Determining the rate of particle interaction can be problematic because of the large number of coupled interactions and potential reactions involved. However, a probabilistic solution to this aggregation can be derived without having to solve the master equation by applying the stochastic probability solution of Gillespie [3]. This solution permits the prediction of the M species in a sequential Monte Carlo simulation based on the probability density function of a given reaction (R_m) occurring in a time increment between t+τ and t+τ+dτ ($P(\tau, \mu)$) and where:

$$k'_{XY} = P_{XY} \cdot P(\tau, \mu)$$

Where

$$P(\tau, \mu) = P_1(\tau) \cdot P_2(\mu \mid \tau)$$

And

$$P_1(\tau) = a \cdot e^{-\tau a} \quad \text{Where} \quad a = \sum_{\mu=1}^{M}\left(j_\mu\,\frac{k'_\mu}{V}\right)$$

Therefore

$$\tau = \frac{1}{a}\ln\left(\frac{1}{R_1}\right) \quad R_1 \in Uniform\{0 < R < 1\}$$

and

$$P_2(\mu \mid \tau) = \frac{j_\mu\,\dfrac{k'_\mu}{V}}{a}$$

Therefore

$$\mu \equiv \sum_{v=1}^{\mu-1}\left(j_v\,\frac{k'_v}{V}\right) < R_2 a \le \sum_{v=1}^{\mu}\left(j_v\,\frac{k'_v}{V}\right)$$

$$R_2 \in Uniform\{0 < R < 1\}$$

Where j_μ is the number of distinct molecular reactant combinations for reaction μ found to be present at time t

and is principally the product of the concentration of the reactants

2.2 Interactions and Reactions

Problems in prediction are further compounded by: 1) the inherent variability in P_{XY}, and 2) that P_{XY} will change with changes in the particles in manners related to, but not functionally consistent with, their size, relative surface area ratios and the nature of previous reaction events. This introduces a second tier of n-dimensional variability to predicting the behavior of nanomaterials in the environment the extent of which is going to be dependent on the physical and surface chemical properties of the material under consideration.

A rational approach to predicting P at a given instant in a chain reaction would be to consider the change in the thermodynamics of reactants and the products, which then go on to become the reactants in subsequent events. This can be simplified into a 2-step event. The first involves the probability of activation in the interaction (denoted as P_{XYact}). The probability of activation is a function of the probability density of the activation energy relative to the probability distribution of momentary kinetic energy (total energy minus potential energy over a period of t+τ and t+τ+dτ). The resulting P_{XYact} can be defined then as the probability of that the combined kinetic energies of X and Y in a per unit time exceeds the activation energy of X+Y as follows:

$$X + Y \rightarrow XY^*$$

$$P_{XYact} = e^{\frac{2E_{XY}-E_{XY^*}}{kT}} \quad E_{XY} \in N\left\{\mu = \frac{kT}{3\pi\eta r_X r_Y}, \sigma = \sqrt{\mu}\right\}$$

Where

$$E_{XY^*} = G_{XY^*} - (G_X + G_Y)$$

The free energies (G) of the reactants can be approximated as the combined kinetic energies of X and Y. The free energy of the activation product (G_{XY^*}) in this case is the repulsive energy between the active surface moieties upon the two nanoparticles as they approach each other.

For the proportion of interactions where the combined kinetic energy of X and Y meet or exceed the potential energy of E_{xy^*}, there is the second binary probability with regards to the outcome of the reaction. Of the subpopulation of interaction with sufficient energy accruing between t+τ and t+τ+dτ, a portion will result in a stable aggregation of XY ($P_{XY'}$), with the remainder undergoing an elastic collision and returning to X + Y. The probability is directly related to the net change if free energy between XY and the sum of free energies for X+Y: the greater the reduction in free energy (i.e. the more exothermic the reaction), the greater the value of $P_{XY'}$. This can be quantified as follows:

$$P_{XY'} = \frac{k'_{XY'}}{k'_{XY}' + k'^{-1}_{XY'}}$$

Therefore

$$\ln(P_{XY'}) = \frac{-G_{XY'}}{-G_{XY}' - (G_X + G_Y) + k'^{-1}_{XY'}}$$

Where k' represents the respective reaction rates of the reactions given interaction.

Combining the two stages of the interaction and reaction, a final stochastic relation can be developed as follows:

$$P_{XY} = P_{XYact} \cdot P_{XY'}$$

Therefore

$$k'_{XY} = P_{XYact}(\tau) \cdot P_{XY'}(\tau) \cdot P(\tau, \mu)$$

With the characterization of these two reaction factors, in combination with the before-defined probability of interaction, it is now possible to predict the rate and therefore the equilibrium conditions for the reaction of nanoparticles with themselves and other components of the environment based on their thermodynamics.

3 RESULTS AND DISCUSSION

The ultimate utility of modeling nanoparticle kinetics is to permit the prediction of the behavior of nanomaterials in a manner that has become typical for anthropogenic materials in the environment. Over the past several years, regulatory risk assessment for registration, emissions and releases have come to rely on predictive modeling. In the United States, programs under the Toxic Substances Control Act (TSCA) and the Federal Insecticide, Fungicide and Rodenticides Act (FIFRA) require specific physicochemical data for a substances in order to predict its fate, transport, and impact. Likewise, the European Union, under the new Registration, Evaluation, and Authorization of Chemicals (REACH) will rely heavily on comprehensive models like the EU System for the Evaluation of Substances (EUSES) to determine conditions for registration.

Typical inputs for these types of *a priori* models include properties such as solubility, lipid partition, Henry's Law coefficients, etc. The problem with nanomaterials is that the mass and corresponding energies renders many of these environmental parameters meaningless when applied to what are in effect molecular entities with masses 2-3 times greater than typical chemicals considered. Furthermore, surface properties inferred by considerations such as compositional architecture and crystalline structure alter the chemical properties such that comparisons to solublized forms are extremely misleading.

Solubility and partition are the most important state properties in estimating the fate and transport of materials in the aqueous environment. In most cases, these properties are indicative of the nanomaterial's ability to form metastable emulsions in aqueous solutions. The stability of these nanoparticle aqueous emulsions (10-100 nm) is very high (Figure 1). At 298 K, the increased buoyancy provided by the small particle size results in 98 to 100 percent of an initial amount added remaining in equilibrium suspension even at densities as high as density of 11.5 g/cm3 (equivalent to elemental lead). Density of the material has little effect on the stability of the suspension until the particles reach the 75-300 nm radius range (Figure 2). From this inflection range, the proportion in suspension declines dramatically to near zero between 500 to 1000 nm radii.

The unique environmental transport of materials in nanoparticle form will only occur so long as the nanoparticles remain as nanoparticles. For compliance purposes, the standard filter size for defining the filtered fractions is 0.45 um [4]. Therefore, for a nanoparticle to be excluded from the soluble fraction and be considered a constituent of the particulate fraction, the particles must aggregate to an effective radius in excess of 450 nm. For a 100 nm particle, this will require between 5 and 90 aggregation reactions depending on the geometry of the particles. For a 50 nm particle, exclusion from the filtered fraction will require between 9 and 750 aggregation reactions.
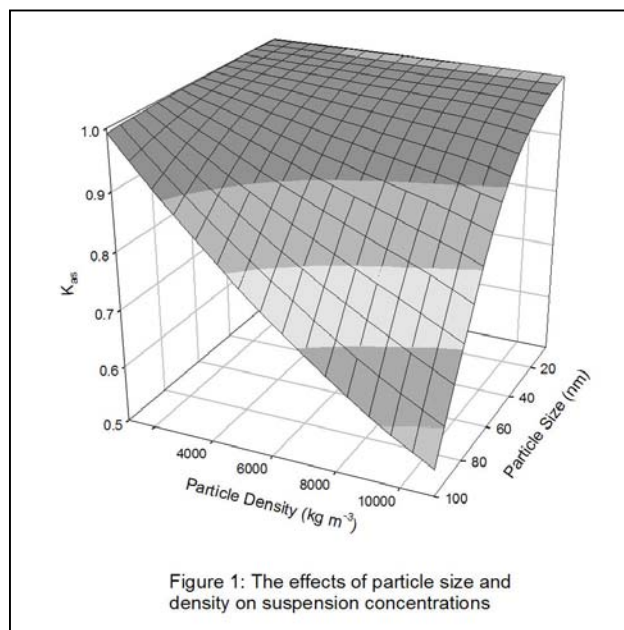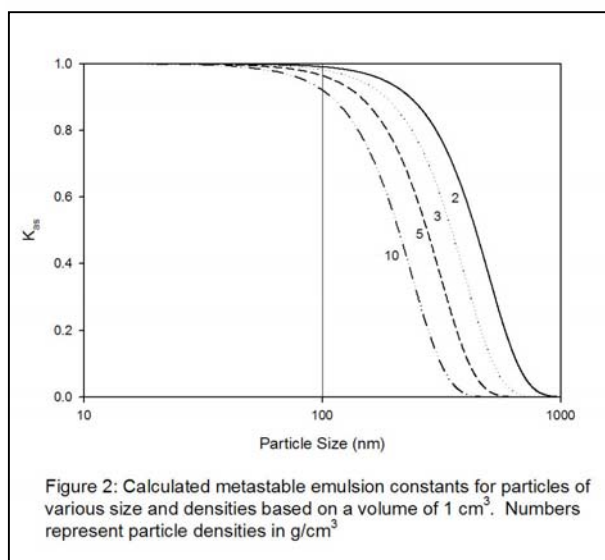

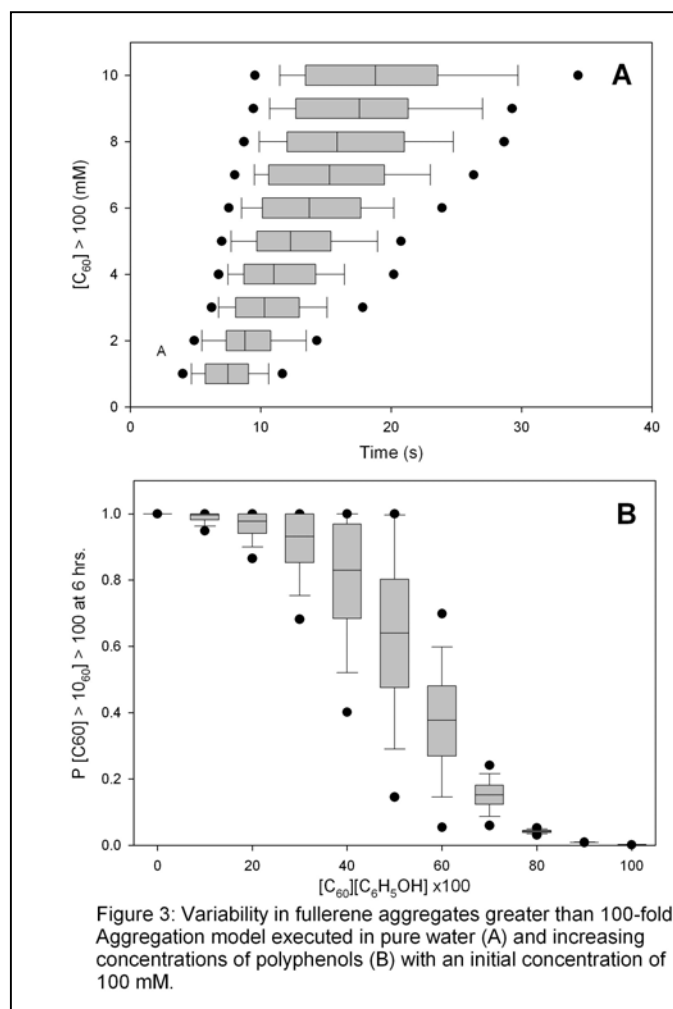Figure 1: The effects of particle size and density on suspension concentrations

The collision kinetics that governs the aggregation/precipitation reactions constitutes a series of interdependent reactions governed by their own rate constants and dependent on the time-dependent concentration of the precursors. When predicting the

Figure 2: Calculated metastable emulsion constants for particles of various size and densities based on a volume of 1 cm^3. Numbers represent particle densities in g/cm^3

Figure 3: Variability in fullerene aggregates greater than 100-fold. Aggregation model executed in pure water (A) and increasing concentrations of polyphenols (B) with an initial concentration of 100 mM.

behavior of multiple interconnected constituents of varying size, this forms and extremely complicated Markov chain with a large number of potential solutions. By using the stochastic probability approach, it is possible to determine to only the most likely rate, but also the expected variability as well as the impact of other environmental constituents. For example, Figure 3 represents the predicted aggregation of a C_{60} fullerene in a pure aqueous solution under conditions of no energetic inhibition (P_{XYact}=1), and highly exothermic advantage ($P_{XY'}(\tau)$=0.865). The situation changes if the dispersed fullerenes are introduced to an aqueous solution containing polyphenol (mimicking humic acid). As demonstrated in Figure 3a, the initial kinetic mimic those of pure fullerene. However, as the nanomaterials interact with the polythenols, both the P_{XYact} and $P_{XY'}(\tau)$ increase resulting in a broadening on the particle distribution and the introduction of an asymptotic limit on the attainable aggregated size. The higher the relative concentration of the polyphenols to fullerene concentration, the slower the aggregation and small the size limit (Figure 3b). This type of particle stabilization was recently reported by Hyung et al. [5].

4   CONCLUSIONS

With the increase in the use of nanomaterials, there will come an increase in their introduction into the environment. Current approaches to modeling fate, transport, and impact of materials in the environment are based on properties such as vapor pressure and solubility. Nanomaterials that have very low solubility and very low vapor pressures can none the less be highly mobile by virtue of their ability to form metastable emulsions in water are aerosols in air. Further compounding the problems of prediction, it appears that natural materials in the environment can both increase or reduce the metastability of nanomaterial's thereby significantly affecting this time-course behavior. The

predictive approach presented here can be applied to predict the concentration of these emulsions both with regard to the initial stability in suspension as well as stability of these suspensions with time. However, it will require knowledge of the thermodynamics of the material that can be attained either from molecular modeling or experimental observations. By including these properties in predictive modeling efforts, it should be possible to better determine the potential risks associated based their behavior within environmental media.

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