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Statistical Thermodynamic Description of Heteroaggregation between Anthropogenic Particulate Matter and Natural Particles in Aquatic Environments

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ABSTRACT: Aggregation is a key process in understanding the fate and transport of anthropogenic particulate matter, namely, nanoparticles and microplastics, in aquatic environments. Recent research has subdivided aggregation into two processes: homoaggregation, where two like particles aggregate, such as two fragments of microplastic, and heteroaggregation, where two unlike particles aggregate, such as a nanoparticle and sediment. Of the two processes, heteroaggregation is generally assumed to be more important because anthropogenic particles are much less concentrated than their naturally occurring counterparts. This assumption remains largely untested in many natural settings,



and most aggregation models discount the process of disaggregation entirely. To address these deficiencies, we created a statistical thermodynamic aggregation model to predict the steady-state size distribution of any two-particle system, accounting for homoaggregation, heteroaggregation, and disaggregation. The results of the model confirm that homoaggregation is likely a negligible process for the fate of nanoparticles and microplastics. However, the model predicts that heteroaggregation will be incomplete, with at least 10% of the nanoparticles or microplastics remaining unaggregated (i.e., monomeric form) even under favorable bonding conditions and large concentration disparities (i.e., surrounded by a far greater concentration of secondary particles). Our model also predicts that heteroaggregation is influenced by the magnitude of the enthalpy of bonding (H_b) between the anthropogenic particle and the larger natural particle. While these predictions require experimental verification, the implications of this study highlight the critical need to consider and carefully examine disaggregation in the context of heteroaggregation (and homoaggregation) of anthropogenic and natural (in)organic particles.

KEYWORDS: heteroaggregation, aggregation, nanoparticles, microplastics, disaggregation

INTRODUCTION

Anthropogenic particulate matter has emerged as the latest class of potential contaminates to catch the public's attention. Concern for nanoparticles is based on the novel properties of this material and/or the potential effects of intentional or unintentional exposure of nanoparticles to humans and the environment.^{1–6} More recently, public concern has shifted to microplastics and their effect on organisms that dwell within rivers, lakes, and oceans.^{7–10} Despite the wide range of materials that are encompassed in "anthropogenic particulate matter", all of these materials are thought to share similar processes that control their fate.^{7,11,12} A key fate-determining process shared between all types of anthropogenic particulate matter as well as natural particulate matter is aggregation, whereby particles stick together.^{7,12,13}

Much of the scientific understanding of aggregation has been developed through application of a kinetic model, generally referred to as the von Smoluchowski equation

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \frac{1}{2} \sum_{i=1}^{i=j-1} \alpha_{i,j} K_{i,j} n_i n_j - n_k \sum_{i=1}^{i=\infty} \alpha_{i,k} K_{i,k} n_i \tag{1}$$

where the concentration of particles of a given size fraction (n) changes with a rate constant equal to the product of the frequency of collisions (K) and the probability of attachment (α) , which is a value between 0 and 1 that is proportional to the energy barrier impeding attachment.^{14–17} This relatively simple equation has proven to be a powerful tool to understand the aggregation of nanoparticles and microplastics. Both experimental and theoretical studies have yielded two important conclusions with respect to the aggregation of anthropogenic particulate matter, which can be used to guide ongoing work. First, homoaggregation or aggregation between two like materials (e.g., two silver nanoparticles) is negligible.^{7,18–20} Second, heteroaggregation or aggregation between two unlike materials (e.g., a nanoparticle/microplastic

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© 2021 The Authors. Published by American Chemical Society and natural sediment) occurs completely and nearly instantaneously under environmentally relevant surface water conditions. $^{19,21-23}$

These two conclusions are based on the expectation that the concentration of anthropogenic particulate matter is dwarfed by that of natural particles in the environment. Therefore, no matter how large the energy barrier and correspondingly small α , the sheer number of natural sedimentary particles will overcome any energy barrier leading to heteroaggreation.^{24–26} However, these predictions are extrapolated from experiments on the early aggregation processes and a theoretical model that does not account for disaggregation.^{15,18,27,28}

Disaggregation, while considered an important part of natural systems, is difficult to study experimentally using the kinetic approach. The simple two-term model, shown in eq 1, when expanded to account for heteroaggregation becomes a six-term model, with the majority of the added terms having no theoretical basis for estimation.²⁹ Additionally, the experimental methods to study aggregation are optimized for the early stage of aggregation to measure α when disaggregation is a small factor because there are few aggregates to disaggregate. As a result, the process of disaggregation is often ignored in studies of the aggregation of anthropogenic particulate matter. However, disaggregation has been experimentally observed in homoaggregated nanoparticles, after the addition of natural organic matter, reduction of ionic strength, and/or addition of shear stress.^{30–35} Additionally, there is experimental evidence that aggregate breakup occurs for 0.25-2 μ m carboxylated polystyrene from the primary energy minima predicted by the extended DLVO theory.^{36,37} Furthermore, as a result of the larger size of microplastics, disaggregation is predicted to have a greater role in the environmental fate of these larger anthropogenic particles.

One way around the challenge presented by the kinetic aggregation model is to use a different model, specifically a maximum entropy model, to examine disaggregation. There have been several different formulations of the maximum entropy model over the years.^{38–41} All of these stem from the recognition that if aggregation experiments run for a sufficiently long period of time, then a self-preserving size distribution is reached, indicating that a steady-state form or a dynamic equilibrium is achieved.^{38–41} Interest in the maximum entropy model has waned over the years and dropped into obscurity in part because the formulators of the method were reliant on analytical expressions of the model that could not account for the effect of floc strength.⁴²

A new formulation, independent of the past maximum entropy effort, was recently proposed by Sokolov et al. and analytically refined by Kätelhön et al.^{43,44} Their model does not rely on entropy alone. Rather, entropy is used to drive the solution of the Gibbs free energy equation (G = H - TS), where the enthalpy term (H) essentially accounts for the floc strength. Additionally, an analytical solution is no longer required for the maximum entropy model because computers can now be used to numerically maximize the entropy of the system.^{43,44}

Sokolov et al. demonstrated that their model is capable of adequately predicting the homoaggregated size distributions for a wide range of nanomaterials, such as Ag, Au, Fe₂O₃, and Bi₂O₃.^{43,45-48} However, the major drawback of their approach is the use of a brute-force method to find a solution, testing every possible combination for a given number of monomers and available aggregation states.⁴³ This leads to extremely long

computational times for even relatively simple systems. Another drawback to the model of Sokolov et al., as formulated, is that it can only describe homoaggregation.⁴³ It cannot be use to describe heteroaggregation, which is the process of primary interest to studies of anthropogenic particles in the environment.^{12,26}

Herein, we lay a theoretical foundation to study heteroaggregation of anthropogenic particles, like nanoparticles and microplastics. This is accomplished by generalizing the maximum entropy model proposed by Sokolov et al. to include a description for the aggregation of two unlike materials (e.g., a nanoparticle and natural particle).⁴³ Our heteroaggregation model was built in a number of steps. First, we replaced the brute-force computational method of Sokolov et al. with a technique of constrained optimization.⁴³ Our new computational approach yielded results identical to the original homoaggregation model in a fraction of the time.⁴³ Next, we introduced a second particle into our model to assess the effect that two particles have on one another even when they cannot make contact. The final step in the construction of the full aggregation model was to allow the two particles to directly interact. The sensitivity of the full model parameters was tested and yielded some expected predictions (e.g., negligible homoaggregation of anthropogenic particles) as well as a few surprises (e.g., incomplete heteroaggregation of anthropogenic particles to natural particulate matter). Utilization of this approach provides a simple model for understanding nanoparticle and microplastic aggregation that intrinsically accounts for disaggregation, a process that may be important to the fate and transport of emerging anthropogenic particles.

METHODS

The governing equations of the homoaggregation model proposed by Sokolov et al. are presented in Table 1.⁴³ These equations were implemented in MATLAB version 2018b using the constrained optimization routines of the software. To determine the solution, we vectorized each of the equations in Table 1 and used the interior point algorithm to minimize the Gibbs free energy of the system under the assumption of Sokolov et al. that the aggregates form in a close-packed arrangement of monomers.⁴³

Three modifications to the homoaggregation model were required to transform it to describe heteroaggregation. (i) The definition of N (the total number of particles in the system) was changed to be the sum of the particles in all available aggregation states, which is consistent with the definition of the mole fraction used in the original homoaggregation model. (ii) The constraint function was modified to have an additional constraint, namely, the conservation of the initial number of both the primary anthropogenic particle (A) and the secondary natural heteroparticle (B). (iii) The $H_{\rm b}$ term in the Gibbs free energy equation becomes a multiple value vector with one enthalpy of bonding for each bond type, e.g., $\overline{H}_{b} = \{H_{b_{A-A}}, H_{b_{A-A}}\}$ $H_{\mathbf{b}_{A-B^{\prime}}}$, $H_{\mathbf{b}_{B-B}}$. A consequence of this modification is that n_i (the number of bonds in an aggregate) becomes a matrix containing the integer number of bonds of each type in an aggregate. In keeping with the close-packed aggregate assumption used by Sokolov et al., a maximum aggregation state was set at the tetramer (i = 4).⁴³ This maximum is necessary because, under the close-packed assumption, the pentamer (i = 5) and all larger aggregation states are degenerate (i.e., having multiple possible arrangements of the A and B particles).

Table 1. Governing Equations of the Statistical Thermodynamics Model, Where G Is the Gibbs Free Energy in kJ mol⁻¹, H Is the Enthalpy in kJ mol⁻¹, T Is the Temperature in Kelvin, and S in the Entropy in kJ K⁻¹ mol^{-1 a}



^{*a*} N_i is the number of aggregates in the *i*th aggregation microstate; H_b is the enthalpy of bonding with units kJ mol⁻¹ contact point⁻¹ implemented as a vector with one H_b for each type of bond in the model {A–A, A–B, and B–B}; n_i is the number of each bond in the *i*th aggregation microstate; k_b is the Boltzmann constant; N is the total number of particles in the system; and x_i is the mole fraction of the aggregates in the *i*th aggregation microstate defined as $x_i = N_i/N$. In the constraint function, **i** is the total number or particles in each aggregate, **A** is the number of secondary natural heteroparticles in a given aggregate, $N_{A,B}$ is the number of aggregates containing some number of A and B particles (e.g., $N_{2,1}$ describes the AAB aggregate), and N_{int} is the initial number of monomers of a given type A or B, respectively.

While the model was being tested, we found that the numerical solver did not always converge to a solution as the number of particles A and B became more disparate. This was likely due to a feature scaling problem. To solve this problem, two model variants were implemented to ensure a solution. The first variant called the "iterative" implementation was based on the observation (presented in the Results) that the more concentrated of the two particles adopts the homoag-gregation distributions reported by Sokolov et al.⁴³ Therefore, the homoaggregated distribution of the more concentrated particle could be found first and then used as the initial condition for the full heteroaggregation model. This iterative implementation thereby solves the feature scaling problem by making the model more likely to start in the correct attractor basin.

The second variant, called the "simplified" implementation, solves the feature scaling problem by treating the secondary particle (B) as a monomer whose aggregation state is of no interest. This reduces the number of terms that the optimization algorithm needs to solve the feature scaling problem and makes the energy minimization entirely dependent upon the feature of interest, that is, the primary particle (A). This change is due to the observation (also presented in the Results) that the more concentrated particle behaves as if it were the only particle in the system. Figure 1 shows the heteroaggregation system with the close-packed aggregation states and the aggregates allowed by each implementation (iterative and simplified).



Figure 1. Two-dimensional representation of allowed aggregation states, where blue circles (labeled A) represent the primary anthropogenic particle and the larger orange circles (labeled B) represent the natural heteroparticle (not to scale). All microstates are allowed in the iterative model. The simplified model uses only the enclosed microstates (dotted line) and the secondary B particles, which are treated as monomeric. Note that the term "microstate" describes the specific configuration of a thermodynamic system as a result of thermal fluctuations and may be used for both micro- and nanoscale particles. In subsequent figures, a homodimer is shown as AA or BB, a heterodimer is shown as AAB or ABB, etc.

RESULTS

Application of the Numerical Solver to the Homoaggregation Model. A statistical thermodynamic heteroaggregation model was developed over the course of several steps that were evaluated on the basis of how the model worked and the results produced at each step. First, a numerical solver was added to the method of Sokolov et al., replacing their brute-force solution.⁴³ The numerical solver successfully reproduced their results, as evidenced by SI Figure 1 and SI Table 1 of the Supporting Information, which replicate the data of Figure 5a and Table 3 in the original paper by Sokolov et al. For comparison, the difference between the values is reported in SI Table 2 of the Supporting Information.

The benefit of using the numerical solver is clearly illustrated by the time that it took to find a solution. Beginning with an initial 200 monomers, Sokolov et al. reported finding solutions for their entropy-only model in 180 and 750 min for the $i_{max} =$ 10 and 11 aggregation states, respectively.⁴³ By comparison, our numerical optimization solved each problem in under 1 s. More impressively, the numerical optimization technique does not have a time penalty for increasing the initial number of monomers, allowing for more realistic concentrations to be modeled.

Entropy-Only Heteroaggregation. The next step in building the full heteroaggregation model was to add a second particle to the system. This was done in multiple stages, starting with the case that prevented heteroaggregation, allowing only homoaggregation to take place. This step permitted us to isolate the effect of varying the relative concentration of the two particles. Because heteroaggregation was prevented, we expected both particles to form homoaggregation distributions at maximum entropy. However, this was not the case, as illustrated in Figure 2. Instead, the two different particles appeared to influence one another even though they could not aggregate.



Figure 2. Results of the iterative heteroaggregation model under entropy-only, non-interacting conditions (i.e., no A–B bond is possible), where the relative concentration of the primary anthropogenic particle (A) and the secondary natural particle (B) are varied. Results are expressed as a percentage of $N_{\rm int}$, the initial number of monomers of the respective particle in each aggregate. For example, if there are initially 1000 particles of A with 175 homodimers, then the percentage of $N_{\rm int}$ is calculated as (175 homodimers) × (2 monomers/homodimer)/1000 initial monomers = 35%.

When the two particles are in equal concentrations $(N_{\rm b}/N_{\rm a})$ = 1), both particles have the same distribution (Figure 2). However, this distribution is not the homoaggregation distribution reported by Sokolov et al.; instead, it is slightly skewed to the monomeric state.⁴³ Figure 2 shows that, as the concentration of B increases, it is less affected by A (i.e., the other particle in much lower concentration) and its distribution becomes equivalent to the homoaggregation distribution found by Sokolov et al.43 Meanwhile, the distribution of A becomes increasingly more monomeric as the concentration of B increases (see Figure 2). These observations suggest that, in mixed particle systems, homoaggregation is unlikely for the less concentrated particle (A) because there are simply too few of these particles to collide with one another. Varying the initial conditions of the model (e.g., setting both particles to the predicted optimal homoaggregation distributions) did not alter the results, which continued to adopt the same distributions shown in Figure 2.

In the next step, we ran the full heteroaggregation model under entropy-only conditions, allowing for both homoaggregation and heteroaggregation. The von Smoluchowski equation (i.e., the kinetic model; eq 1) predicts that the less concentrated particle (A) should become fully heteroaggregated (i.e., no free or homoaggregated particles) as the relative concentration becomes more disparate. This is because any energetic barrier to aggregation should be overcome as a result of the dwarfed particle concentration $(N_b \gg N_a)$. However, our entropy-only heteroaggregation model shows a different result.

The results of the model (Figure 3) show that, when the two particles are in equal concentrations $(N_{\rm h}/N_{\rm a}=1)$, then their distributions mirror one another. In this case, about 36% of each particle is homoaggregated, 24% of each particle is heteroaggregated, and 40% of each particle is in the monomer form. When the concentration of the B particles is increased $(N_{\rm b}/N_{\rm a} = 10, 100, 1000, \text{ and } 10\,000)$, the B particle reverts to the homoaggregation distribution with a negligible percent in the heteroaggregated form. Importantly, this observation supports both the simplified and iterative implementation of the full heteroaggregation model. When the two different particles are in disparate concentrations, the more concentrated particle B behaves as if it was the only particle present and its distribution does not change in response to the other particle (A). In this instance of entropy-only conditions, B maintains the entropy-only homoaggregation distribution found by Sokolov et al.43

Meanwhile, the A particle does decrease to 0% homoaggregation, which is also predicted with eq 1. However, heteroaggregation does not increase to 100%. Instead, a maximum of 45% of particle A becomes heteroaggregated, with these aggregates containing only a single A particle. The remaining 55% of particle A is predicted to be in the monomeric form (e.g., see Figure 3a). The key prediction here is that entropy could overcome the sheer number of natural particles relative to anthropogenic particles.

Assessing the Role of the Enthalpy of Bonding (H_b). The results described above address the role of entropy on particle distributions within an aggregate. The next step is to assess the enthalpy of bonding (H_b). Sokolov et al. tested only three possible values for H_b , with the 5 kJ mol⁻¹ contact point⁻¹ being the most extreme value of H_b .⁴³ Following their lead, we ran our simplified model with the dimer (i = 2) as the maximum permitted aggregate size and varied $H_{b_{A-B}}$ and $H_{b_{A-B}}$ between -5 and 5 kJ mol⁻¹ contact point⁻¹ in steps of 500 J mol⁻¹ contact point⁻¹.

Figure 4 displays the percentages of A in each aggregation state (A, AA, and AB) for relative concentrations $N_b/N_a = 1$ and $N_b/N_a = 100$. These results reveal that bonding conditions play a significant role in the end results of the predictive model.



Figure 3. Results of the complete iterative heteroaggregation model under entropy-only conditions, where the relative concentration of the primary particle (A) and the secondary natural heteroparticle (B) are varied. (a) Relative percentage in $N_{A,int}$ the initial number of monomers of A. (b) Relative percentage in $N_{B,int}$, the initial number of monomers of B. Categories not shown in either panel have none of their respective monomers (0%). Results are expressed as a percentage of N_{int} , the initial number of monomers of the primary particle in each aggregate. Note the difference in the *y*-axis scale compared to Figure 2.



Figure 4. Assessing the role of enthalpy of bonding (H_b) . Results of the simplified heteroaggregation model for the relative concentrations $N_{int,B}/N_{int,A} = 1$ and $N_{int,B}/N_{int,A} = 100$ as the enthalpy of bonding of both the A–A $(H_{b_{A-A}})$ and A–B $(H_{b_{A-B}})$ bonds are varied between –5 and 5 kJ mol⁻¹ contact point⁻¹. Results are expressed as the percentage of initial primary particle monomers present in each aggregation microstate.

Table 2. Maximum Percentage of Primary Particle A in Each Aggregation State in the Range from -5 to 5 kJ mol⁻¹ Contact Point⁻¹ for Each Relative Concentration of the Two Particles from $N_{int,B}/N_{int,A} = 1$ to 1000^{a}

	$N_{\rm int,B}/N_{\rm int,A} = 1$	$N_{\rm int,B}/N_{\rm int,A} = 10$	$N_{\rm int,B}/N_{\rm int,A} = 100$	$N_{\rm int,B}/N_{\rm int,A} = 1000$
А	84.4	87.5	88.2	88.3
AB	64.9	87.1	88.2	88.3
AA	70.2	40.0	9.5	1.1

^{*a*}The maximum percentage of A was always found at the H_b (enthalpy of bonding) values of {5, 5, 0} kJ mol⁻¹ contact point⁻¹; the AB maximum was always found at the H_b values of {5, -5, 0} kJ mol⁻¹ contact point⁻¹; and the AA maximum was always found at the H_b values of {-5, 5, 0} kJ mol⁻¹ contact point⁻¹.

Positive $H_{\rm b}$ values shift the distribution to the monomer, whereas more negative $H_{\rm b}$ values shift the distribution to an aggregated state. Figure 4 also supports the prediction that homoaggregation of anthropogenic particles is negligible in most environments. Less than 10% of particle A is predicted to be homoaggregated under even the most favorable conditions $(H_{\rm b} = \{-5, 5, 0\} \text{ kJ mol}^{-1} \text{ contact point}^{-1}; \text{ relative}$ concentration $N_{\rm b}/N_{\rm a} = 100$). This percentage drops further as the difference in the particle concentration becomes more disparate. For example, Table 2 shows that only 1.1% of particle A is homoaggregated at $N_{\rm b}/N_{\rm a} = 1000$. Even under the most favorable bonding conditions proposed by Sokolov et al.⁴³ $(H_{\rm b} = \{-5, -5, 0\} \text{ kJ mol}^{-1} \text{ contact point}^{-1})$, our model predicts incomplete aggregation, with 10% of the A particles remaining as monomers in the $N_b/N_a = 100$ test. In short, our results for the bonding enthalpy disagree with the prediction of von Smoluchowski's kinetic model (eq 1) of complete heteroaggregation.

The results of our model displayed in Figure 4 and Table 2 allowed for only the dimer aggregation state. To test whether this condition impacted the results, the simplified model was run for trimers, removing the close-packed assumption. This means that the two A particles in the ABA trimer are not touching one another. For these simulations, we also set H_b to $\{0, -5, 0\}$ kJ mol⁻¹ contact point⁻¹, thereby maximizing the chance for heteroaggregation.

Figure 5 shows the results of this model as a function of the relative concentration (N_b/N_a) . These data reveal that the additional aggregation state does not make a difference at high relative concentrations, which is expected for most environments (i.e., smaller concentration of anthropogenic particles relative to natural sedimentary particles). This result can be explained using the same rationale for the lack of formation of homoaggregated dimers. The heteroaggregates create, in essence, another low-concentration particle class. Because both classes (A and AB) are in low concentrations, they are unlikely to encounter one another to aggregate and form larger structures.

DISCUSSION

The process of aggregation, the joining of two or more particles into one, is a phenomenon studied across a wide number of disciplines. Recent studies on the fate of nanomaterials in aquatic environments have documented a need to be more specific with aggregation terminology, a finding that is also shared by those studying microplastics.^{7,11,49} Specifically, aggregation should be split into two distinct processes: (i) homoaggregation or aggregation between two like particles (e.g., two microplastic particles) and (ii) heteroaggregation or aggregation between two unlike particles (e.g., a nanoparticle and a clay particle). However, splitting these two processes significantly increases the complexity of the kinetic aggregation model, the most commonly used aggregation model (see eq 1).

To counter this complexity, researchers have attempted to simplify their models by explicitly or implicitly ignoring homoaggregation and disaggregation processes, with the assumption that both processes provide only minor contributions. Evidence in support of this assumption comes from fitting a simplified model to experimental results obtained under conditions where disaggregation is unlikely (e.g., reaction in an unstirred beaker). However, there is recent acknowledgment that these examples hide complexity and may not hold under more realistic conditions.¹² Additionally, more studies have been conducted that show natural and anthropogenic particles do, in fact, readily break up (i.e., disaggregate) under turbulence and changes in ionic strength, which may then lead to increased homoaggregation or monomeric anthropogenic particulate matter.^{30–34}



Figure 5. Percentage of A monomers in each category for the simplified model with an $i_{max} = 3$ run at $H_b = \{0, -5, 0\}$ kJ mol⁻¹ contact point⁻¹, maximizing the heteroaggregation potential, as a function of the relative concentration. These data illustrate that adding more aggregation states does not shift the distribution toward increased aggregation.

In this paper, we have created a simple model that can account for disaggregation as well as the two different forms of aggregation (homo and hetero) by extending and generalizing a previously described maximum entropy model for aggregation.^{43,44} Instead of the focus on the early aggregation process, the steady-state or equilibrium state is used to provide more generalizable insight on where anthropogenic particulate matter will ultimately end up. While our model is developed from a recent description of the maximum entropy model for nanoparticles, we hypothesize that it will be applicable for a variety of other systems.

Implications of Using a Numerical Solver. Perhaps the greatest advance of the model proposed by Sokolov et al. was the use of computing power to maximize entropy rather than relying on analytical solutions.³⁸⁻⁴³ However, the method that they developed was a bit crude because it determined the maximum entropy solution by brute-force testing every possible combination of particles and aggregates. While this approach does indeed guarantee an optimal solution, it has one significant drawback, computation time. For example, Sokolov et al. reported that a solution for 200 initial particles with 9 possible aggregation states was found after 30 min.⁴³ This time increased to 180 min with 10 aggregation states and to 750 min with 11 aggregation states.⁴³ Expanding this model for heteroaggregation with disparate particle concentrations would therefore be untenable using the brute-force approach. Instead, another solution is necessary, namely, a numerical solver that finds the maximum entropy using algorithmic means.

The results of our numerical solver (SI Figure 1 and SI Table 1 of the Supporting Information) are not only in agreement with the brute-force solution by Sokolov et al., but our solutions were also determined in a fraction of the time (1 s versus 750 min for 11 aggregation states).⁴³ It is worth noting that there are some subtle differences in the solutions. First, the solution from the numerical solver will never be able to find the exact integer solution, like Sokolov et al., because they used a "test every combination" approach.⁴³ This is because numerical solvers do not find integer solutions; instead, they determine a decimal solution that is close to the integer solution. As an example, in the case of $i_{\text{max}} = 2$ and $N_{\text{int}} = 200$, the numerical method finds N_1 as 89.44 and N_2 as 55.28, while the "test every combination" approach yields $N_1 = 90$ and $N_2 =$ 55. The difference between the two results is minor but significant enough to create error at low N_{int} even though the Gibbs free energy of the numerical solution is slightly larger than that of the integer solution.

As $N_{\rm int}$ grows, the two solutions converge because the numerical solution finds the asymptotically correct solution. In the example above, when $N_{\rm int}$ is increased to 2000, the numerical method finds N_1 = 894.42 and N_2 = 552.78 and the integer solution finds N_1 = 894 and N_2 = 553. Thus, the numerical optimization achieves an overly precise solution, but the effect of this precision decreases as the number of particles increases.

It is possible that the numerical solver will not determine the true global statistical maximum entropy because it converges to a local extreme or fails to converge because of poor initial conditions. This issue is magnified as the number of possible aggregation states increases. In fact, the iterative and simplified models were implemented to mitigate this problem. The approach of the iterative solution is based on the observation that, as the concentration of the secondary particle increases relative to the primary particle, the secondary particle reverts to the homoaggregation distribution (as shown in Figure 2). Therefore, the homoaggregation distribution of the secondary particle can be used in the initial condition, which limits the amount of change necessary to find the solution. This also makes the model more likely to start in the correct attractor basin.

The simplified approach, on the other hand, works by reducing the number of possible aggregation states. The benefit of both solutions is that the final solution is in essence dictated by changes to the distribution of the primary particle. However, both solutions do not necessarily ensure that the true global maximum is found, although they do make it more likely to find the optimal solution. A guaranteed true maximum can be found using global optimization techniques, namely, sampling a wide number of initial conditions and comparing the outcomes.

Role of the Enthalpy Term. The addition of the enthalpy term is another advance that Sokolov et al. made to previous maximum entropy models. The model no longer maximizes the entropy of the system, rather it minimizes the Gibbs free energy of the system.⁴³ This important change was only considered in passing by Sokolov et al. noting that aggregation is promoted with a more negative enthalpy of bonding, whereas lower aggregation is observed with a more positive enthalpy.⁴³ Our work expands on this by demonstrating that the enthalpy of the bonding term is key to the development of a more generalized model for heteroaggregation (see Figure 4).

a more generalized model for heteroaggregation (see Figure 4). The enthalpy term $(H = \sum_{i=1}^{i_{max}} N_i H_b n_i)$ consists of three components: H_b , the enthalpy of bonding; n_i , the number of contact points in an aggregate; and N_i , the number of aggregates of size *i*. N_i is the component of interest determined by the numerical solver and, therefore, requires no further discussion. The other two components H_b and n_i are both chosen by the modeler and, therefore, require a more thorough consideration.

The n_i term requires an assumption to be made about how particles in an aggregate are held together. Two limiting cases were proposed by Sokolov et al.: the linear chain model and close-packed aggregate model.⁴³ Herein, to allow for easier comparison to Sokolov et al., we choose the close-packed model.⁴³ The choice to focus on the close-packed limit was made because the linear chain model yields results in multiple degenerate configurations after i = 2, whereas the close-packed model generates multiple configurations after i = 4. However, neither limiting case is a mandatory choice, and other, perhaps more realistic, aggregate geometries can be used. These might include ballistic, diffusion-limited, or reaction-limited assumptions of the aggregate structure and use of a non-integer number of bonds to account for degenerate aggregation states.⁵⁰⁻⁵² The results from these models could absolutely be used to inform assumptions relevant to n_i . For example, Teichmann et al. found that, as aggregate size grows, most particles are attached to two other particles.⁵⁰ While this is the case for homoaggregation, the models could be adapted to heteroaggregation and with a large enough sample of aggregates deriving mean values of n_i for smaller aggregates.

Unlike the n_i term, one cannot make assumptions to determine the H_b term. Therefore, the enthalpy of bonding represents the largest unknown in the model. This is important to appreciate because H_b has a significant effect on the final distribution that is predicted by the model (see Figure 4). When the model was run with H_b set to $\{0, -10, 0\}$ kJ mol⁻¹ contact point⁻¹ for $N_{int,B}/N_{int,A} = 100$, the percent

unaggregated dropped to 1.7%, which is much closer to complete heteroaggregation (Figure 4).

The solution space used in Figure 4 was adopted from Sokolov et al., who chose the range seemingly arbitrarily. It is therefore unknown whether the -5 to 5 kJ mol⁻¹ contact point⁻¹ range is too large or too small for real-world systems.⁴³ This range seems reasonable based on the work of Michels et al. for microplastics. They found incomplete heteroaggregation of marine biogenic particles with only 40–90% of the microplastics included in aggregates, depending upon the test conditions.⁵³ Importantly, these percentages are in line with predictions from our statistical thermodynamic model for H_b values ranging from entropy-only to close to -5 kJ mol⁻¹

Speculating more precisely on the true range of $H_{\rm h}$ is mostly futile because the model has only been directly tested for homoaggregation, which has already been described adequately by the entropy-only distribution $(H_{\rm b} = 0 \text{ kJ mol}^{-1})$ contact point⁻¹). This offers no additional insight on the expected range other than it will include 0 kJ mol⁻¹ contact point⁻¹. We would expect that, for stable systems, $H_{\rm b}$ would be ≥ 0 because 0 was shown to be appropriate for stable distributions by Sokolov et al. and increasing $H_{\rm b}$ shifts the distribution toward a monomeric distribution.⁴³ In unstable systems, we expect $H_{\rm b}$ to be <0 (i.e., negative), which would be expected to predict a greater degree of aggregation. In the specific case of oppositely charged particles, $H_{\rm b}$ is predicted to be $\ll 0$ (i.e., very negative), to the point where the model would predict the monomers to be completely aggregated. Additionally, we hypothesize that $H_{\rm h}$ may be analogous to the sticking coefficient, α , in the kinetic model (eq 1) in that it is a property intrinsic to the system governed by the DLVO or extended DLVO theory. This would mean that the usual caveats of varying surface charge, pH, ionic strength, presence of natural organic matter or extracellular polymeric substances, etc. are likely to change $H_{\rm b}$ for a given system.

The challenge then becomes how to experimentally determine $H_{\rm b}$, so that its magnitude can be assessed and compared to theory. The first option would be to collect heteroaggregation data using a single-particle technique, like nanoparticle tracking analysis or particle impact coulometry, as performed to validate the homoaggregation data.^{43,45-48} Then, the resulting distribution was fit with $H_{\rm b}$ as an additional fitting parameter. While this technique is possible it has several drawbacks. It is, in essence, laying on a second numerical optimization to produce the distribution, which adds another layer of complexity and source of failure. Single-particle techniques also suffer from a "needle in a haystack" problem as a result of the anthropogenic particles being in low concentration under realistic environmental concentrations.¹² Additionally, the particle impact coulometry technique, while a promising analytical technique advocated for by others (e.g., Sokolov et al.), is currently facing reliability issues that are still being debated in the literature and requires significant skill in electrochemistry to obtain meaningful results.54-58 An alternative, more straightforward approach would be to measure $H_{\rm b}$ directly using atomic force microscopy, where one could measure the energy of the surface-tip bond.^{59,60} This method has the added benefit of being able to directly compare experimental measurements to the DLVO theory.⁵

CONCLUSION

We have developed a statistical thermodynamics model focusing on the steady-state distribution that shows promise toward developing a more realistic, mechanistic-based description of nanoparticle and microplastic heteroaggregation and, therefore, fate in aquatic environments. Our model confirms a key conclusion of the much used kinetic aggregation modeling (eq 1). That is, homoaggregation of anthropogenic particulate matter is negligible because concentration disparities are so great that two nanoparticles (or two microparticles) are unlikely to interact with one another. Our model also provides another interesting prediction that runs counter to the kinetic aggregation model. Here, we show that heteroaggregation does not necessarily go to completion, even under favorable bonding conditions, where secondary particle (e.g., natural sediment particle) concentrations are in excess of the primary particle (e.g., nanoparticle or microplastic). This would mean that these anthropogenic particles (nanoparticles and microplastics) are unlikely to settle to stream beds with sediment. Instead, nano- or microparticles may be transported through river systems to the ocean. If nothing else, this new model should serve to remind us that disaggregation, a process that is often overlooked, is critical and certainly worth more directed and careful study when considering both homo- and heteroaggregation.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspace-chem.0c00318.

Use of our numerical approach rather than the test every combination approach to replicate Table 3 from Sokolov et al. (SI Table 1), difference of values determined using our numerical approach minus the test every combination approach shown in Table 3 from Sokolov et al. (SI Table 2), and agglomerate distribution of the closepacked Gibbs free energy model found using the numerical optimization solver at three different enthalpies of bonding (SI Figure 1) (PDF)

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