

Lock-and-key dimerization in dense Brownian systems of hard annular sector particlesWade D. Hodson¹ and Thomas G. Mason^{1,2,*}¹*Department of Physics and Astronomy, University of California, Los Angeles, California 90095, USA*²*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, USA*

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We develop a translational-rotational cage model that describes the behavior of dense two-dimensional (2D) Brownian systems of hard annular sector particles (ASPs), resembling C shapes. At high particle densities, pairs of ASPs can form mutually interdigitating lock-and-key dimers. This cage model considers either one or two mobile central ASPs which can translate and rotate within a static cage of surrounding ASPs that mimics the system's average local structure and density. By comparing with recent measurements made on dispersions of microscale lithographic ASPs [P. Y. Wang and T. G. Mason, *J. Am. Chem. Soc.* **137**, 15308 (2015)], we show that mobile two-particle predictions of the probability of dimerization P_{dimer} , equilibrium constant K , and 2D osmotic pressure Π_{2D} as a function of the particle area fraction ϕ_A correspond closely to these experiments. By contrast, predictions based on only a single mobile particle do not agree well with either the two-particle predictions or the experimental data. Thus, we show that collective entropy can play an essential role in the behavior of dense Brownian systems composed of nontrivial hard shapes, such as ASPs.

DOI: [10.1103/PhysRevE.94.022124](https://doi.org/10.1103/PhysRevE.94.022124)**I. INTRODUCTION**

Homodimer formation has been observed for many different types of molecules, ranging from simple acetic acid [1] to highly complex proteins [2]. In particular, many kinds of proteins, such as the structural coat proteins of viruses [3,4], and functional enzymes, such as organophosphorous hydrolase [5], form homodimers. In such complex molecular systems, site-specific interactions between monomers, by mechanisms such as hydrogen bonding, can play important roles in dimer formation and stability. By contrast, in Brownian systems of hard colloidal particles, the core shapes of constituent particles and entropy maximization essentially determine the system's structure and its phase behavior at a certain particle density [6,7]. For instance, certain particle shapes, which have shape-complementary convex and concave regions, can form composite lock-and-key dimer structures [8]. For hard particles, the simplest type of dimer is the lock-and-key homodimer composed of two identical monomers that mutually interpenetrate, such that the convex portion of one particle enters the concave portion of the other and vice versa. Because attractions are absent in hard particle systems, emergent dimer structures can only be maintained over long times in highly crowded environments. In such crowded environments, the osmotic pressure exerted by neighboring particles inhibits the separation of two monomers that have interpenetrated to form a dimer.

Recently, lithographic fabrication of monodisperse dispersions of microscale annular sector particles (ASPs) [8–12] and formation of two-dimensional (2D) Brownian systems of particles at high densities that have effectively hard interactions [13,14] using roughness-controlled depletion attractions [15–18] have enabled direct visualization of dimerization in two dimensions [9]. Here, we investigate the degree of dimerization of colloidal ASPs in dense 2D Brownian systems using a translational-rotational cage model simulation that is similar to prior cage model simulations of dense Brownian systems of

hard rhombs [19,20] and hard tri-stars [21]. Using a collision detection routine that detects when two ASPs overlap, this simulation enumerates accessible translational and rotational microstates associated with either one or two mobile ASPs surrounded by a static cage of ASPs. This cage structure approximates the average local structure around the central mobile ASP(s) and sets the system's overall density, similar to cage models of hard spheres [22,23]. Once these accessible microstates have been determined, key thermodynamic properties of the system can be calculated using basic principles of statistical mechanics [24,25]. This direct cage modeling approach provides insight into how many local degrees of freedom must be included in order to obtain reasonably accurate predictions for the collective behavior of the dense hard particle system; such insight is not typically provided by many-particle simulations based on Brownian or molecular dynamics [26].

ASPs represent an interesting class of shapes that can range from slender partial rings to pie wedges [27]. Here, we consider a monodisperse dispersion of uniform ASPs that resemble partial rings or C shapes. The shape and size of an ASP can be characterized by the following three parameters: an inner radius R_i , an outer radius R_o , and an opening angle ψ , as defined in Fig. 1(a). Thus, the perimeter of an ASP is set by two aligned concentric circular arcs, each having an angular range $2\pi - \psi$, and two radial line segments, each having a length $R_o - R_i$, which connect the ends of the arcs. If R_o is chosen to set a characteristic particle length scale, then only two parameters completely define this class of ASP shapes: R_i/R_o and ψ . For certain ranges of these parameters, two monomer ASPs have the capacity to dimerize in mutual lock-and-key configurations. We define mutual lock-and-key dimerization to occur when a portion of one ASP makes contact with an imaginary dashed line extending between the ends of the inner circular arc of the other ASP and vice versa. Examples of configurations of two proximate ASPs that are not dimerized are shown in Figs. 1(b) and 1(c). However, in the example configuration shown in Fig. 1(d), a portion of one ASP penetrates into the interior cavity of the other ASP and vice versa, so this is a mutual lock-and-key dimer.

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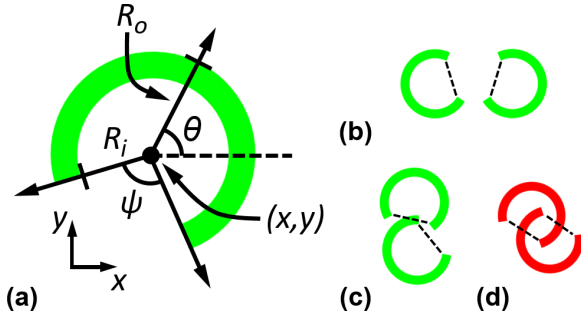


FIG. 1. Schematics of an annular sector particle (ASP) and the geometrical condition defining mutual lock-and-key dimerization of two ASPs. (a) Shape and size parameters characterizing an ASP: R_i and R_o are the inner and outer radii, respectively; ψ is the opening angle. Coordinates x and y define the center of the ASP with respect to the origin of a fixed reference frame. θ is its orientation angle, with respect to the x axis, based on a ray from the center of the circular arcs to a point that is midway between the ends of the ASP's two arms. (b) Two separate monomer ASPs: no portion of a first ASP intersects with the imaginary dashed line defining the opening boundary of the concave interior of a second ASP and vice versa. (c) Two proximate ASPs: a first ASP does intersect with the imaginary dashed line of a second ASP, but the second ASP does not contact the imaginary dashed line of the first ASP. (d) Two proximate ASPs in a mutually interpenetrating lock-and-key dimer configuration. Mutually interpenetrating lock-and-key dimerization occurs when a portion of the perimeter of one ASP intersects with the imaginary dashed line spanning the inner opening of the other ASP and vice versa. This geometric definition for dimerization of nonoverlapping ASPs can be readily determined using a collision detection routine. This collision detection routine is based on a combination of routines which detect the intersection of two circular arcs, a line segment with a circular arc, and two line segments.

In order to understand how the process of dimerization is influenced by factors such as particle shape and particle density, we implement a model of either one mobile ASP or two mobile ASPs within a fixed cage of neighboring ASPs. In this simulation, the space of accessible positions and angular orientations (i.e., accessible microstates) of up to two mobile ASPs is discretized and systematically explored using a collision detection routine, written in *Mathematica* (Wolfram Research). This routine also determines which accessible microstates of mobile ASP(s) correspond to mutual lock-and-key dimer configurations of the two central sectors, using a geometric test criterion [see Figs. 1(b)–1(d)]. These simulations are executed over a range of particle area fractions ϕ_A , a quantity related to the average density of the cage, and over a range of values of the particle shape parameters R_i/R_o and ψ . This range of shape parameters includes values which match the parameters of ASPs that have been studied experimentally. Although dimers of ASPs are known to have positive and negative chiral senses, here, we model dimerization having only a single chiral sense since the results for the mirror image of the dimer cage structure are the same. Because the model only relies on an average local short-range structure around a given pair of mobile ASPs, we show that this model for the cage reasonably describes the main thermodynamic features of dense systems of ASPs that

form in racemic proportions and are therefore disordered at medium and long range. Although the ASPs are strictly hard particles, dimers can be compressed over a fairly wide range of ϕ_A above the dilute limit, and this leads to an interesting dependence of the equilibrium constant K of the dimerization reaction as a function of applied 2D osmotic pressure Π_{2D} .

The results of these cage model simulations are given in terms of the total number of accessible microstates Ω and the number of accessible dimer microstates Ω_D for the mobile ASP(s). These values can be used to compute a variety of physical quantities of interest, including the probability of dimerization P_{dimer} , K of the lock-and-key dimerization reaction, and Π_{2D} of the thermalized system. Predictions of these quantities are found to match closely with experimental measurements of ASPs, without introducing adjustable parameters. Given this success, we extend results of these cage model simulations to ranges of shape parameters that have not been explored yet experimentally. Moreover, these simulation results demonstrate the importance of accounting for the collective microstates of pairs of mobile ASPs, not just a single ASP, in order to accurately reproduce certain key features of the hard ASP system.

II. METHODS

In order to study dimerization in systems of ASPs, a translational-rotational cage model is implemented in *Mathematica*, similar to previous simulations used to study colloidal dispersions of particle shapes such as rhombs [20] and tri-stars [21]. This cage model has been developed to treat either a single central mobile ASP or, alternatively, a pair of central mobile ASPs. While the two-ASP calculation requires significantly more computational time, it also provides more realistic predictions because it includes the most basic contribution to the collective entropy of the system.

At each different value of ϕ_A , we build a static cage of ASPs that describes the average local structure around a central pair of ASPs, whether dimerized or not. To do this, we define and solve a set of equations that equalizes all spacings between densely configured pairs of ASPs that are uniformly positioned, oriented, and diluted, as shown in Fig. 2. Such equalized spacings between ASPs create cage configurations that approximately maximize the accessible microstates for cage ASPs if they were allowed to explore different configurations. At higher ϕ_A , the cage ASPs are all dimerized, whereas at lower ϕ_A , the cage ASPs are separated monomers. The cage effectively defines a noncircular central cavity in which the two central mobile ASPs are located, and the accessible microstates of these mobile ASPs are constrained by nonoverlap with regard to each other and also the cage ASPs. This approach for defining the cage is taken for computational convenience since such idealized cage structures, while providing a reasonable approximation of an average cage structure at a certain density, do not incorporate the randomness in chirality and orientation of dimerized ASPs that have been observed in experiments. To reduce computational time, collision detection between central mobile ASPs and certain outer cage ASPs (e.g., uppermost two ASPs and lowermost two ASPs shown in Fig. 2) can be eliminated, except at lower ϕ_A towards the dilute limit, in which case

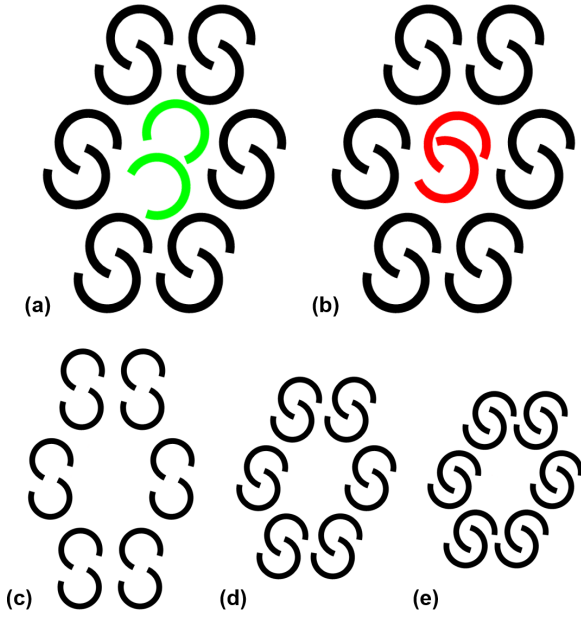


FIG. 2. Cage configurations limiting motion of the central ASPs over a range of values of particle area fractions ϕ_A : $R_i/R_o = 0.75$ and $\psi = 95^\circ$. Static cage ASPs are shown in black. Examples of two central mobile ASPs at $\phi_A = 0.263$ in (a) a monomer configuration (green or light gray) and (b) a dimer configuration (red or dark gray). Example cages generated at ϕ_A : (c) 0.180, (d) 0.263, and (e) 0.340.

potential collisions with additional outer cage ASPs are also checked. For most values of ϕ_A that we consider, collisions of central mobile ASPs with only the eight cage ASPs closest to them need to be checked. Two central mobile ASPs can have a configuration corresponding to either noninterpenetrating monomers [e.g., Fig. 2(a)] or to mutually interpenetrating lock-and-key dimers [e.g., Fig. 2(b)]. Examples of cages, showing the central cavity, at several different ϕ_A values are shown in Figs. 2(c)–2(e).

Given two fixed shape parameters R_i/R_o and ψ , as well as ϕ_A , the cage model simulation for two mobile ASPs is implemented as follows. First, a spatial configuration of the cage is defined to match the given ϕ_A . We then discretize the six-dimensional space of all possible positions and orientations of the two central ASPs, which yields a set of all possible microstates, some of which might be accessible to the central ASPs without any overlap. For each microstate in this set, a collision detection algorithm determines whether this microstate corresponds to a physically accessible state of the two central ASPs. Here, an accessible state is one for which the central ASPs do not overlap with each other and also do not overlap with any cage ASPs. In addition, if a state is found to be accessible, then it is also tested to determine if the configuration corresponds to a lock-and-key dimer, as defined in Fig. 1(d). The typical output of the cage model simulation, for particular values of R_i/R_o , ψ , and ϕ_A , consists of the total number of accessible microstates Ω and the number of accessible dimer microstates Ω_D . The number of accessible monomer (i.e., nondimer) microstates is simply $\Omega_M = \Omega - \Omega_D$. If desired, the entire list of accessible states in the six-dimensional phase space can also be generated. To preserve the accuracy of the results while reducing computational time,

we use a finer discretization of the phase space at larger ϕ_A and a coarser discretization at lower ϕ_A . The resulting numbers of microstates are appropriately rescaled with respect to a fixed six-dimensional volume representing the entire phase space of microstates, so that the results of simulations executed at different discretizations can be meaningfully combined.

This two-particle cage model simulation is performed over a range of shape parameter values for R_i/R_o from 0.65 to 0.8 and for ψ from 70° to 120° . For each pair of parameters in this range, Ω and Ω_D are computed for values of ϕ_A between 0.08 and 0.48. Specifically, the simulation is run for $R_i/R_o = 0.75$ and $\psi = 95^\circ$ in order to compare the simulation results with experimental data [9] which have been gathered for ASPs with these shape parameter values. The lower limit of this range of ϕ_A values is set by the escape of central ASPs from the cage, and the upper limit is set by the highest packing density above which overlap of ASPs would always occur.

In addition, for $R_i/R_o = 0.75$ and $\psi = 95^\circ$, a modified version of this simulation, having only a single central mobile ASP, is performed in order to compare with measurements and results of the two-particle simulations. In this single-particle version, one central ASP is held at a fixed position and orientation corresponding to the cage configuration, while the other central ASP is moved and tested for nonoverlap. Collision detection is used to determine the numbers of accessible and dimer microstates based only on the motion of a single central ASP. This single-particle simulation has a reduced three-dimensional phase space and runs very rapidly (time $\sim N^3$, where N represents a number of microstates checked along a given dimension of the phase space). However, as a consequence of its basic assumptions, the single-particle simulation does not include collective entropic effects. By contrast, the two-particle simulation, which has a six-dimensional phase space, runs more slowly (time $\sim N^6$), but it does include collective entropic effects at a basic level. For $R_i/R_o = 0.75$ and $\psi = 95^\circ$ using the two-particle simulation, the average run time to calculate accessible microstates over the entire cage and classify configurations as monomer or dimer is about 5 h on a ThinkServer (Lenovo TS140, Xeon E31225v3 quad-core 3.2 GHz, 4 GB RAM) for 15 different values of ϕ_A .

III. RESULTS AND DISCUSSION

As an example to illustrate accessible microstates of central ASPs in a cage of immobile ASPs, we show transparency overlay plots of the accessible monomer and dimer microstates for a single-particle simulation in Figs. 3(a) and 3(b), respectively. Only some accessible microstates correspond to mutually interpenetrating lock-and-key configurations. The requirement of *mutual* interpenetration is our strict geometrical definition for dimerization; *both* particles must have portions that cross the dashed lines of the other shown in Fig. 1(d). For two-particle simulations, both central ASPs can move within the static cage. This two-particle case is difficult to depict clearly since the transparency overlay plots become smeared over the entire cage.

Over a range of different shape parameters R_i/R_o and ψ , we have calculated Ω and Ω_D , respectively, as a function of ϕ_A . Having determined Ω and Ω_D through collision detection, the equilibrium physical properties of dense 2D Brownian

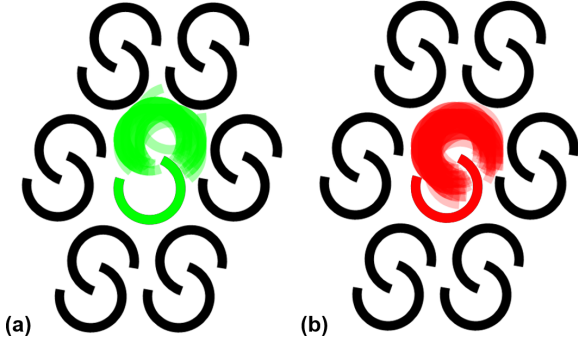


FIG. 3. Accessible microstates of a first central mobile ASP (top) from the single-particle simulation for a fixed position and orientation of a second central ASP (bottom). Here, $R_i/R_o = 0.75$, $\psi = 95^\circ$, and $\phi_A = 0.263$. The location and orientation of the fixed ASP, with respect to a coordinate system located at the geometric center of the cage, are given by $x = -0.05$, $y = -0.5$, and $\theta = 300^\circ$, in units where $R_o = 1$. Transparency overlay plots of accessible microstates corresponding to (a) monomer configurations (green or light gray) and (b) dimer configurations (red or dark gray).

systems of ASPs can be computed for different R_i/R_o and ψ as a function of ϕ_A . The probability of dimerization is simply $P_{\text{dimer}} = \Omega_D/\Omega$, given the assumption of equal *a priori* probabilities for each accessible microstate. Experimentally, this probability can be identified as the fraction of particle pairs which are dimerized. The equilibrium constant K is defined by assuming that separated particle pairs are reactants and dimerized pairs are products. The change in the Gibbs free energy associated with the dimerization reaction of a pair of ASPs is $\Delta G = -k_B T \ln K$, where k_B is Boltzmann's constant and T is the temperature. For hard particle systems, this free energy change is entirely entropic: $\Delta G = -T \Delta S$, where ΔS is the entropy change of this reaction. Applying Boltzmann's definition of entropy between monomer and dimer states of the pair yields $\Delta S = k_B \ln(\Omega_D/\Omega_M)$. After equating these two expressions for ΔG of the reaction, K can be simply deduced as $K = \Omega_D/\Omega_M$. Because the phase space is six-dimensional, corresponding to microstates of two particles regardless of whether or not they have dimerized, this form for K , which can be determined from the simulation results, is equivalent to the experimental K determined by the law of mass action, $K = \phi_{A,D}/\phi_{A,M}^2$ using measured area fractions of dimers $\phi_{A,D}$ and monomers $\phi_{A,M}$, respectively, at the same depth in an equilibrated 2D gravitational column. Moreover, the 2D osmotic pressure Π_{2D} as a function of ϕ_A is given by

$$\Pi_{2D}(\phi_A) = -\frac{k_B T}{2A_p} \phi_A^2 \frac{\partial(\ln \Omega)}{\partial \phi_A}. \quad (1)$$

Here, A_p is the area of a single ASP, and Ω is a function that depends on ϕ_A . Thus, the osmotic equation of state $\Pi_{2D}(\phi_A)$ can be determined by calculating $\Omega(\phi_A)$ from the simulation and then differentiating with respect to ϕ_A .

In prior experiments [9,21], if a system of Brownian hard particles in a 2D column is subject to a uniform gravitational field, then the two-dimensional osmotic pressure can also be expressed in terms of an integral that yields the total effective

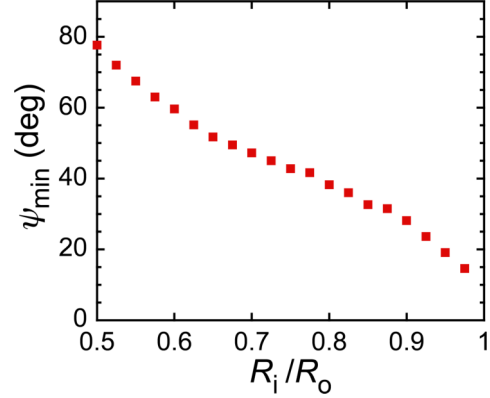


FIG. 4. Calculated minimum value of the opening angle ψ_{\min} of ASP shapes that can dimerize as a function of R_i/R_o . In the region below this curve, dimerization is impossible.

particle mass above a given height z in the column:

$$\Pi_{2D}(z) = \frac{k_B T}{A_p} \int_z^\infty \phi_A(z') (dz'/h_g). \quad (2)$$

This integral depends on a particular thermal-gravitational height h_g associated with the initial exponential increase in particle density as a function of depth within the equilibrated column in the dilute gas-like region. In the prior experiments [9], Π_{2D} has been obtained by extracting h_g from a curve fit of $\phi_{A,M}(z)$ and then integrating using Eq. (2). However, some minor inaccuracy in the experimental h_g could have resulted from the curve fitting method that was employed since this value depends on the functional form and the range of z used in the fit. Here, we refit the experimental data for $\phi_{A,M}(z)$ using a simple exponential form, including only the most dilute gas-like region, and carefully check the correlation coefficient to see how it changes for different ranges of z used in the fit. From this, we determine a more accurate value of $h_g = 4.35 \mu\text{m}$, which is lower than the prior reported value of $h_g = 5.6 \mu\text{m}$ [9], which included an additional point at z closer to the reaction zone; including this extra point reduces the correlation coefficient, and thus, it should not have been included. Using the more reliable value of $h_g = 4.35 \mu\text{m}$, we follow the same procedure in calculating Π_{2D} for the experiments and use these values when comparing with the simulation results for Π_{2D} from Eq. (1). We emphasize that the simulation results for $\Pi_{2D}(\phi_A)$ in Eq. (1) are independent of any value used for h_g in determining an experimental $\Pi_{2D}(\phi_A)$.

Geometry limits the range of values of R_i/R_o and ψ over which dimerization of two separate monomer ASPs is physically possible while keeping both ASPs in the plane while translating and rotating them. Dimerization can readily occur when the opening angle is large and the aspect ratio is sufficiently slender. Thus, at large ψ and R_i/R_o , dimerization is possible, but as ψ is reduced or as the annular sector becomes thicker, corresponding to smaller R_i/R_o , dimerization is prohibited. These restrictions are quantified in Fig. 4, which displays the minimum value of ψ for which dimerization is possible, given a particular value of R_i/R_o . This value ψ_{\min} has been computed by numerically sampling the space of possible relative positions of two annular sectors for given values of ψ

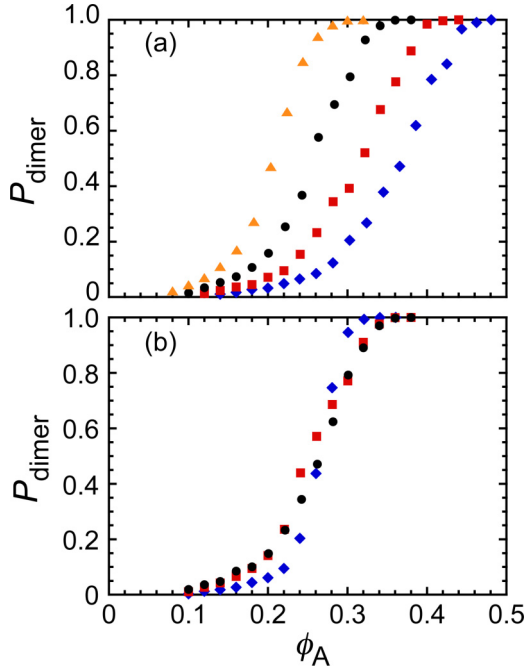


FIG. 5. Predictions from the two-particle cage model simulation of the dimerization probability P_{dimer} . (a) P_{dimer} as a function of ϕ_A at fixed $\psi = 100^\circ$: $R_i/R_o = 0.65$ (blue diamonds), $R_i/R_o = 0.7$ (red squares), $R_i/R_o = 0.75$ (black circles), and $R_i/R_o = 0.8$ (orange triangles). (b) P_{dimer} as a function of ϕ_A at fixed $R_i/R_o = 0.75$: $\psi = 70^\circ$ (blue diamonds), $\psi = 90^\circ$ (red squares), and $\psi = 110^\circ$ (black circles).

and R_i/R_o . Here, we consider dimerization to be physically possible if, in this space of relative positions, there exists an unbroken path between a undimerized configuration and a dimer state. This criterion excludes cases where the annular sectors would have to intersect one another in order to reach the dimer configuration since these states are not physically realizable without lifting one of the annular sectors temporarily out of the plane. Although the simpler test for dimerization displayed in Fig. 1(d) is used for the actual enumeration of microstates in the cage model, the calculation of ψ_{min} offers a definitive geometrical bound on the range of shape parameters for which the cage model remains meaningful.

Computed values of P_{dimer} using the two-particle simulation over a range of R_i/R_o and ψ are displayed in Fig. 5. This probability is sensitive to changes in the slenderness of the ASPs, determined by R_i/R_o , as shown in Fig. 5(a). As R_i/R_o is increased towards unity, corresponding to increasingly slender ASPs, dimerization can occur more readily at lower ϕ_A . The thickness of the ends of the arms of ASPs relative to the opening angle is thus a key parameter related to insertion and dimerization; this controls the changes in ϕ_A associated with the rise in P_{dimer} in Fig. 5(a). By contrast, in Fig. 5(b), we show that $P_{\text{dimer}}(\phi_A)$ for fixed $R_i/R_o = 0.75$ is not as sensitive to values of ψ over a limited range that corresponds to C shapes. In this case, the differences between the curves are not as large, but the transition from low values of P_{dimer} to high values is much sharper for $\psi = 70^\circ$ than for $\psi = 110^\circ$.

For $R_i/R_o = 0.75$ and $\psi = 95^\circ$, near values that correspond to experiments [9], computed values of P_{dimer} , K , and

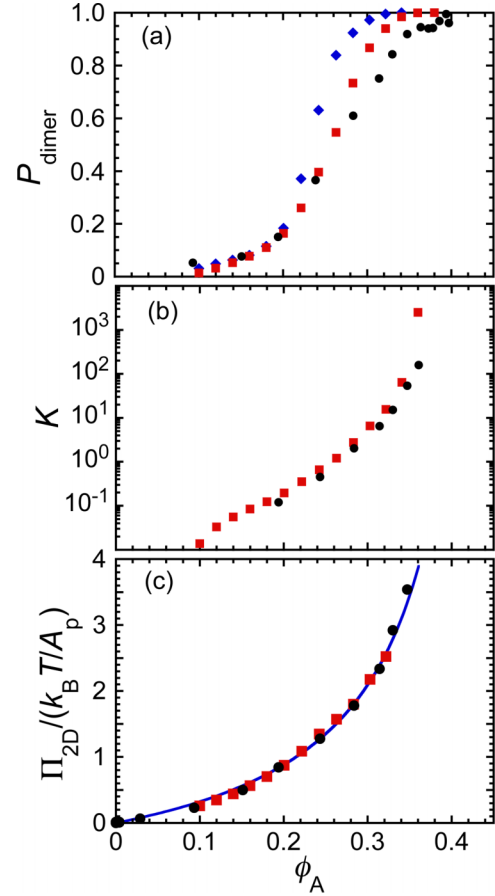


FIG. 6. Results of cage model simulations and experimental data as functions of ϕ_A . (a) Probability of dimerization P_{dimer} : experiments (black circles), two-particle simulations (red squares), and one-particle simulations (blue diamonds). (b) Equilibrium constant K of the dimerization reaction [same symbols as in (a)]. (c) Scaled 2D osmotic pressure Π_{2D} [same symbols as in (a)]. Line: fit to numerical results using Eq. (3) (see text).

Π_{2D} from two-particle simulations are plotted as functions of ϕ_A in Figs. 6(a), 6(b), and 6(c), respectively. We also show experimentally measured values of these quantities [9]. Figure 6(a) includes the values of P_{dimer} determined by the one-particle simulation, in which one of the two central ASPs is fixed in position and orientation. We find good agreement between the experimental data and the two-particle simulation results for P_{dimer} and K for $R_i/R_o = 0.75$ and $\psi = 95^\circ$. Small differences between experiment and simulation are noticeable at ϕ_A greater than 0.28 for P_{dimer} and at ϕ_A greater than 0.34 for K . These differences at high ϕ_A arise primarily because a small but non-negligible population of monomers becomes trapped in the experimental system, whereas the simulation assumes complete dimerization in the local cage. In the experimental system, diffusion of isolated trapped monomers in the crowded environment of dimers is extremely slow, and this kinetically inhibits further dimerization reactions of monomers that could lead to perfect dimerization. Moreover, the one-particle simulation performs poorly compared to the two-particle simulation in predicting the probability of dimerization, as shown by the larger departure from the experimental

data in Fig. 6(a). Similar disagreement of the one-particle simulations in comparison with two-particle simulations and experiments is also observed for K and Π_{2D} . By contrast, the two-particle simulations of K and Π_{2D} nearly match the experimental results without any adjustable parameters over a large range of ϕ_A , as shown in Figs. 6(b) and 6(c), respectively. At the highest $\phi_A = 0.36$ shown, the two-particle simulation of K is much higher than the experimental K ; this is predominantly a consequence of trapped monomers in the experiments, which causes a reduction in the experimental K . In Fig. 6(c), we have not reported simulated values of Π_{2D} at $\phi_A = 0.34$ and $\phi_A = 0.36$ because the discretization chosen for the simulations was not sufficiently fine to provide a large ensemble of accessible microstates. In addition, corner rounding, a consequence of diffraction in the experimental lithographic production of the particles, can cause the area fraction associated with the divergence in Π_{2D} to be different in the experiments than in the simulations, where no corner rounding is present. Thus, overall, the two-particle simulations agree reasonably well with experimental results, except at very high ϕ_A , where trapped monomers are present in the experiments. This indicates that it is necessary to consider two mobile central ASPs, not a single central mobile ASP, in a static cage in order to obtain a reasonable representation of the entropy of the system. Consequently, we focus only on two-particle simulation results for the remainder of this section.

The two-dimensional osmotic pressure varies linearly as a function of ϕ_A for low particle area fractions in the limiting case of an ideal gas, and it diverges at a maximum packing area fraction. This suggests the following functional form for the curve fit of $\Pi_{2D}(\phi_A)$, where adjustable parameter f sets the overall scale and the parameter $\phi_{A,c}$, a critical area fraction, sets the divergence point:

$$\Pi_{2D}(\phi_A)/(k_B T/A_p) = \frac{f\phi_A}{1 - \phi_A/\phi_{A,c}}. \quad (3)$$

We fit the numerical results for the 2D scaled osmotic equation of state using this equation, as shown in Fig. 6(c), yielding very good agreement. Moreover, the fit parameter value of the divergence in the osmotic pressure, $\phi_{A,c} = 0.47 \pm 0.01$, is close to the experimental value $\phi_{A,c} = 0.455$ previously reported [9]. Because we have used a thermal-gravitational height $h_g = 4.35 \mu\text{m}$ here that is based on a more appropriate fit to the first few points of the initial rise of the measured monomer area fraction $\phi_{A,M}(z)$ [9], the coefficient associated with the linear rise of the osmotic equation of state from the fit here is $f = 2.5 \pm 0.1$. This value is the same for both scaled numerical and scaled experimental results. However, corresponding to the different h_g used here, this coefficient is about 30% higher than $f = 1.79$ reported in the prior experimental work. Regardless of the experimental difficulty in precisely determining h_g , the shapes of the numerical and experimental scaled osmotic equations of state agree well over a wide range of particle area fractions.

To show the dependence of K on the scaled Π_{2D} from the two-particle simulations, we determine their values for each ϕ_A in Figs. 6(b) and 6(c) and plot the results in Fig. 7. For $10^{-1} \lesssim K \lesssim 10^2$, we find that K exponentially increases with

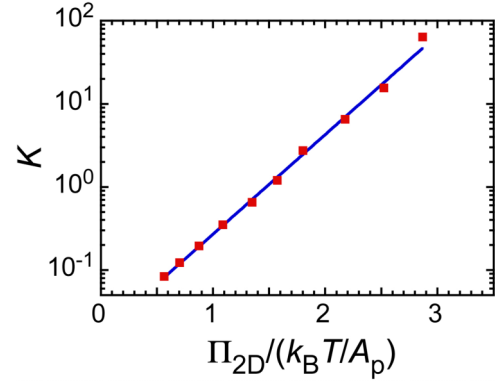


FIG. 7. Two-particle simulation results showing the dependence of the equilibrium constant K of the dimerization reaction as a function of the scaled 2D osmotic pressure Π_{2D} . Solid line: fit using Eq. (4).

scaled Π_{2D} , so we fit this to

$$K = \exp[(\Pi_{2D} - \Pi_{2D,eq})/\Pi_{2D}^*], \quad (4)$$

yielding fit parameter values of scaled $\Pi_{2D,eq} = 1.5 \pm 0.1$ and $\Pi_{2D}^* = 0.36 \pm 0.06$ (i.e., in units of $k_B T/A_p$). For larger values of scaled Π_{2D} beyond the range shown that are closer to the divergence in the scaled $\Pi_{2D}(\phi_A)$, we find that the simulated K departs from this simple exponential dependence and grows even more rapidly as the number of accessible monomer microstates approaches zero. This simulated exponential dependence matches experimental measurements well over the range shown [9]. While our simulations reveal $\ln K \sim \Pi_{2D}$ for the ASP-pair dimerization reaction over a substantial range of scaled Π_{2D} , confirming prior experimental observations, this result could also be equivalently written as an exponential factor in a Poynting pressure correction to the fugacity of nonideal hard ASP particles in a dense system [28]. The capacity of the hard ASPs to form interpenetrating lock-and-key dimer structures that are still compressible below close-packing densities is an interesting feature of this system.

IV. CONCLUSION

Predictions based on the two-particle simulations agree well with experimental measurements made on a 2D Brownian system of ASPs, so a translational-rotational cage model containing two central mobile ASPs adequately captures the primary physical properties over a substantial range of ϕ_A . By contrast, a cage model containing only a single mobile ASP surrounded by a fixed cage does not accurately predict the experimental results. This is an important finding, considering that single-particle translational-rotational cage models have proven to be useful for predicting structures that match experimental measurements reasonably well for other shapes, such as squares, tri-stars, and rhombs [14,19,21]. Therefore, when treating Brownian systems of shapes that can interpenetrate to a significant degree, such as hard ASPs, in order to obtain accurate results using a cage model, a collective form of entropy that goes beyond a single-particle entropy serves as a reasonable starting point. Even so, the

two-particle simulation still contains assumptions that do not exactly reflect the disordered racemic systems of ASPs that have been observed in the experiments. For instance, we have assumed that a perfectly regular dimer lattice is an appropriate cage and that equal spacing between the perimeters of all of the ASPs in the cage reasonably approximates an average local state. This approximation could lead to differences between the predictions and experiments, especially at larger values of ϕ_A . Moreover, because all cage ASPs are fixed and do not fluctuate in the two-particle simulations, we have considered only the six-dimensional phase space of two central mobile ASPs. This assumption of static cage ASPs represents an approximation that neglects other collective contributions to the system's entropy. Our results, based on an assumed local cage structure, could potentially be improved by considering an ensemble of cage structures that more closely mimic the randomness and variety in the chirality and orientation of cage ASPs seen in experiments. Ensemble averaging over many different random cage configurations at the same density could improve predictions of the model towards lower ϕ_A . Even the equations connecting the physical quantities P_{dimer} , K , and Π_{2D} to the numbers of accessible microstates Ω and Ω_D are only strictly valid at thermodynamic equilibrium, and the experimental system contains defects and disorder that indicate the possibility of a state of the system that is not entirely its global minimum-energy ground state. The success of the two-particle cage model of ASPs at reproducing the experimental data without any adjustable parameters suggests that this simplified model accurately captures many key features of the observations, despite these identifiable differences.

Given the success of the two-particle cage model in describing the physical behavior of a real 2D Brownian system of ASPs, simulation results using this two-particle cage model for other values of R_i/R_o and ψ serve as a predictive guide for future experiments on ASPs over a wider range of shape parameters. The predictions that we have presented here,

which span a limited range of R_i/R_o and ψ , have been chosen to correspond to ranges in which the dominant behavior of dimerization is assumed to be present. The cage model that we have presented does not account for other nondimer polymorphs of ASPs, such as polymeric chains, that have also been observed microscopically [9]. More complex modeling approaches would be required to account for a wider polymorphic diversity in reaction products, beyond simple dimers.

Many exciting future directions based on this work can be anticipated. For instance, microstates corresponding to single penetration [Fig. 1(c)] could also be determined as a function of R_i/R_o and ψ , and the population of single-penetration configurations could be compared to those of nonpenetrating and mutually interpenetrating configurations as a function of ϕ_A . In addition, if one considers ASPs having $\psi \approx \psi_{\text{min}}$, one could explore systems for which ψ becomes just large enough to allow dimerization; the behavior of this system should approach that of disks when ψ drops well below ψ_{min} . Likewise, reactions yielding different kinds of local polymorphs, such as chains in addition to dimers, over a broader range of R_i/R_o and ψ could be predicted through simulation and also explored experimentally. Numerically studying the impact of the effective size and shape of the central cavity resulting from a variety of disordered cages, each of which is consistent with the same ϕ_A , could also reveal how sensitive or insensitive the two-particle predictions are to the exact geometries of the cages. Comparisons between the two-particle cage model results and other forms of simulation, such as molecular dynamics or Brownian dynamics, could also be made to determine higher-order contributions to the collective entropy.

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