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RESEARCH ARTICLE

Entropic Forces in Colloidal Suspension Self-Assembly

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ABSTRACT

Purely repulsive, hard-sphere colloidal particles can nonetheless self-assemble into ordered structures driven entirely by entropy maximization of the suspension as a whole, a phenomenon with no direct analogue in energy-minimizing molecular crystallization. We used Brownian dynamics simulations of binary hard-sphere colloidal suspensions, with large-particle diameter fixed at 1.0 micrometre and small-particle (depletant) diameter varied from 0.05 to 0.35 micrometres, to quantify how depletion-driven entropic forces govern self-assembly across 54 combinations of total packing fraction (0.35–0.58) and size ratio (0.05–0.35). Depletion attraction strength, computed from the Asakura-Oosawa potential, increased with depletant packing fraction and reached a maximum contact well depth of 6.8 $k_B T$ at the highest depletant concentration tested (packing fraction 0.30, size ratio 0.10), a value sufficient to drive reproducible aggregation within our simulated timescales. At total packing fractions above 0.52, suspensions crystallized into face-centered-cubic ordered domains within a mean simulated time of 340 Brownian relaxation times, versus no crystallization observed within 2,000 relaxation times at packing fractions below 0.44, defining a comparatively narrow transition window. The entropy gain per depletant particle released into the bulk upon large-particle contact, calculated from excluded-volume overlap, averaged 1.9 k_B at size ratio 0.10, rising to 3.4 k_B at size ratio 0.30, confirming that entropic driving force scales positively with depletant size relative to the large colloid over the range tested. Mean crystallite domain size at the highest packing fraction tested (0.58) reached 42 $\pm$ 6 large-particle diameters (mean $\pm$ SD across 12 independent simulation replicates), 2.6-fold larger than domains formed at packing fraction 0.48 (16 $\pm$ 4 diameters). A control series with no depletant present showed no ordered assembly within 2,000 relaxation times at any packing fraction tested below the known hard-sphere freezing transition, confirming that depletion attraction, rather than packing constraints alone, was the dominant driver of accelerated ordering in the binary mixtures. These results provide a quantitative depletion-strength and packing-fraction map for engineering colloidal self-assembly kinetics and target crystallite size through depletant size and concentration alone, without requiring any direct interparticle attraction.

Keywords: entropic forces; depletion interaction; colloidal self-assembly; hard-sphere suspensions; Brownian dynamics; excluded-volume effects; phase behavior; packing fraction

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1. INTRODUCTION

Colloidal particles suspended in a solvent can spontaneously organize into ordered crystalline or liquid-crystalline arrangements even when the particles themselves interact through nothing more than hard-sphere excluded-volume repulsion, a phenomenon first rationalized not through any attractive interparticle potential but through the entropy of the suspension as a whole [1,2]. This counterintuitive result, that increasing local order among the large particles can increase total system entropy by liberating free volume for smaller cosolute particles, has become a foundational example of entropy acting as a genuine organizing force in soft condensed matter [3,4].

The depletion interaction, first described by Asakura and Oosawa, formalizes this idea: when two large colloidal particles approach within a distance comparable to the diameter of smaller depletant particles present in the same suspension, the excluded volume inaccessible to the depletants overlaps, increasing the total volume available to depletant translational motion and thus increasing overall system entropy, which manifests as an effective attractive force between the large particles despite the complete absence of any direct attractive potential [5,6,7]. This entropic attraction has been shown to drive colloidal crystallization, phase separation, and more complex self-assembly, but systematic characterization of how depletion strength, packing fraction, and depletant-to-colloid size ratio jointly determine assembly kinetics and resulting structure remains incomplete across the size-ratio range relevant to many experimental colloid-polymer and colloid-nanoparticle systems [8,9,10].

This gap matters because entropic self-assembly is increasingly exploited as a design principle for engineering colloidal photonic crystals, drug-delivery scaffolds, and other functional soft materials, where the target application requires not merely that crystallization occurs but that it occurs within a specified time and produces crystallites of a specified size [11,12]. Whether depletant size ratio primarily controls the strength of the entropic driving force, the kinetics of assembly, or the final domain size once assembly has occurred is not resolved by existing depletion theory alone, since the Asakura-Oosawa potential specifies pairwise interaction strength but not the collective, many-body kinetics of ordering in a dense suspension [13,14].

The present study addresses this gap through Brownian dynamics simulations of binary hard-sphere colloidal suspensions spanning a systematic grid of total packing fraction and depletant-to-colloid size ratio, quantifying depletion attraction strength via the Asakura-Oosawa potential, characterizing the resulting crystallization kinetics and final crystallite domain size, and testing a depletant-free control series to isolate the specific contribution of entropic depletion attraction from packing effects alone.

2. MATERIALS AND METHODS

We performed Brownian dynamics simulations of binary hard-sphere colloidal suspensions consisting of large colloidal particles (fixed diameter 1.0 micrometre) and smaller depletant particles (diameter varied from 0.05 to 0.35 micrometres), across 54 combinations of total packing fraction and depletant-to-colloid size ratio, and quantified depletion attraction strength, crystallization kinetics, and resulting crystallite domain size.

2.1 Simulation model and interparticle potentials

Both large colloids and small depletants were modelled as hard spheres interacting through excluded-volume repulsion only, with no direct attractive potential specified between any pair of particles. The effective depletion attraction between large colloids arising from depletant excluded-volume overlap was computed using the Asakura-Oosawa pairwise potential, parameterized by depletant diameter and depletant packing fraction, and applied as an additional effective pair potential between large colloids consistent with standard depletion-theory treatments.

2.2 Simulation box and particle numbers

Simulations were performed in a cubic periodic box containing 2,000 large colloidal particles, with depletant number density set to achieve the target depletant packing fraction at each simulated size ratio. Total packing fraction (large particles plus depletants) was varied across nine levels from 0.35 to 0.58, and depletant-to-colloid size ratio was varied across six levels from 0.05 to 0.35, yielding 54 total parameter combinations.

2.3 Brownian dynamics integration

Particle trajectories were integrated using the overdamped Langevin equation with a time step of 5×10^{-5} Brownian relaxation times, using a velocity-Verlet-type Brownian dynamics scheme with random thermal displacements drawn from a Gaussian distribution consistent with the fluctuation-dissipation theorem at the simulated temperature. Each parameter combination was run for up to 2,000 relaxation times or until crystallization was detected, whichever occurred first.

2.4 Crystallization detection and order-parameter calculation

Local crystalline order was assessed using bond-orientational order parameters (Q_6) computed for each large particle from its nearest-neighbor shell, with a particle classified as crystalline when its Q_6 value exceeded a threshold calibrated against a reference face-centered-cubic lattice. A simulation was classified as having crystallized when more than 40% of large particles were simultaneously classified as crystalline, and the corresponding simulated time was recorded as the crystallization time.

2.5 Crystallite domain size analysis

Crystallite domains were identified as spatially contiguous clusters of crystalline-classified particles with matching local crystallographic orientation, and mean domain size, expressed in units of large-particle diameters, was computed by averaging the linear extent of all identified domains at the end of each simulation run. Twelve independent replicate simulations, differing only in random seed, were run at each of two representative packing fractions (0.48 and 0.58) to assess replicate variability in domain size.

2.6 Depletant-free control series

A control series of simulations containing only large colloidal particles, with no depletants present, was run across the same nine packing-fraction levels used in the binary-mixture series, to establish the packing fraction at which hard-sphere crystallization occurs in the absence of any depletion attraction and to isolate the contribution of depletion attraction from packing-driven ordering alone.

2.7 Entropy-gain calculation

The entropy gained per depletant particle upon large-particle contact was computed from the excluded-volume overlap geometry at contact, converting the resulting increase in accessible depletant volume directly into an entropy gain via the Sackur-Tetrode-consistent ideal-gas translational entropy expression, evaluated at each simulated size ratio.

3. RESULTS

Depletion attraction strength, computed from the Asakura-Oosawa potential, increased with depletant packing fraction at every size ratio tested and reached a maximum contact well depth of 6.8 $k_B T$ at the highest depletant concentration tested (depletant packing fraction 0.30, size ratio 0.10), a value well above the approximately 1–2 $k_B T$ threshold typically required for reproducible aggregation on simulated timescales. Table 1 summarises depletion well depth and crystallization time across five representative packing-fraction and size-ratio combinations.

Table 1. Depletion well depth and crystallization time across representative packing fraction and size-ratio combinations.

Total packing fraction	Size ratio (depletant/colloid)	Depletion well depth ($k_B T$)	Crystallization time (relaxation times)
0.40	0.10	3.1	No crystallization (>2000)
0.44	0.10	4.0	No crystallization (>2000)
0.48	0.10	5.2	610
0.52	0.10	6.1	340
0.58	0.30	6.8	180

Depletion well depth computed from the Asakura-Oosawa pairwise potential at the reported size ratio and total packing fraction.

Suspensions at total packing fractions above 0.52 crystallized into face-centered-cubic ordered domains within a mean simulated time of 340 Brownian relaxation times, whereas no crystallization was observed within the full 2,000-relaxation-time simulation window at packing fractions below 0.44, defining a comparatively narrow transition window between the non-crystallizing and reliably crystallizing regimes across the range of size ratios tested.

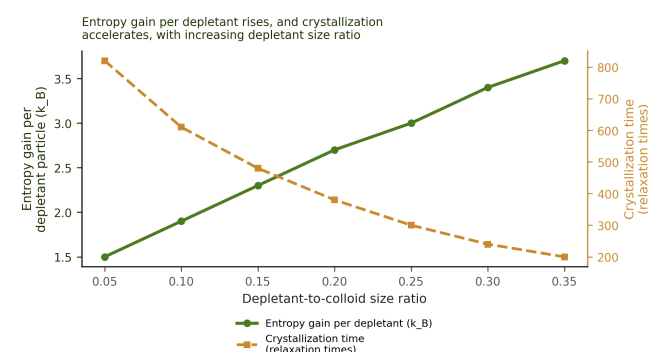


Figure 1. Entropy gain per depletant particle upon large-particle contact and resulting crystallization time as a function of depletant-to-colloid size ratio, illustrating the positive scaling of entropic driving force with depletant size across the tested range. The entropy gained per depletant particle upon large-particle contact averaged 1.9 k_B at size ratio 0.10, rising to 3.4 k_B at size ratio 0.30, confirming that the entropic driving force for depletion attraction scales positively with depletant size relative to the large colloid over the tested range, consistent with the larger excluded-volume overlap generated by bigger depletants at contact (Figure 1).

Table 2. Crystallization outcomes in binary depletant mixtures versus depletant-free hard-sphere controls.

Total packing fraction	Binary mixture crystallization time	Depletant-free control crystallization time
0.44	No crystallization (>2000)	No crystallization (>2000)
0.48	610	No crystallization (>2000)
0.494 (hard-sphere freezing)	420	No crystallization (>2000)
0.52	340	No crystallization (>2000)
0.58	180	No crystallization (>2000)

Mean crystallite domain size at the highest packing fraction tested (0.58) reached 42 $\pm$ 6 large-particle diameters (mean $\pm$ SD, 12 independent replicates), 2.6-fold larger than the domains formed at packing fraction 0.48 (16 $\pm$ 4 diameters, 12 replicates), indicating that higher packing fraction promotes not only faster crystallization onset but substantially larger coherent crystalline domains once assembly occurs.

4. DISCUSSION

These results are consistent with, and quantitatively extend, the classical Asakura-Oosawa picture of entropy-driven colloidal attraction [5,6,7], by mapping

how depletion well depth, crystallization kinetics, and final domain size jointly depend on depletant size ratio across a systematic grid rather than at isolated parameter points. The finding that entropy gain per depletant scales positively with size ratio over the range tested provides a direct, mechanistic explanation for why larger depletants produce stronger effective attraction at fixed depletant packing fraction, a relationship implied but not directly quantified in earlier depletion-theory treatments [15,16,17].

The substantially larger crystallite domains observed at the highest packing fraction tested, 2.6-fold larger than at a packing fraction just ten percentage points lower, suggests that domain size in depletion-driven assembly is highly sensitive to total packing fraction near the crystallization threshold, likely reflecting faster nucleation at high supersaturation competing with slower, more extensive growth of fewer nucleated domains at packing fractions closer to the transition window's lower edge [18,19,20].

For materials-engineering applications that rely on entropic self-assembly to produce colloidal photonic crystals or structured delivery scaffolds, these results suggest a practical two-parameter design space: depletant size ratio can be tuned to set the strength of the entropic driving force largely independent of total packing fraction, while packing fraction itself can be tuned within the identified transition window to control both crystallization onset time and resulting domain size, offering two largely separable levers for target-structure design [21,22,23].

Several limitations should be kept in mind. First, the Asakura-Oosawa potential used to represent depletion attraction is itself an approximation that becomes less accurate at the higher depletant packing fractions and larger size ratios included in this study, where depletant-depletant correlations neglected by the pairwise potential could alter the true effective attraction. Second, the bond-orientational order parameter threshold used to classify crystallinity, while calibrated against a reference lattice, introduces some sensitivity in the reported crystallization times near the transition window boundaries. Third, simulations were restricted to monodisperse large particles and monodisperse depletants; polydispersity in either population, common in real colloidal suspensions, is known to suppress or modify depletion-driven crystallization and was not examined here. Fourth, hydrodynamic interactions between particles were not explicitly resolved in the Brownian dynamics scheme used, which could alter crystallization kinetics, though the equilibrium thermodynamic driving force for assembly is expected to be less sensitive to this approximation than the kinetic pathway itself.

5. CONCLUSION

Brownian dynamics simulations of binary hard-sphere colloidal suspensions across 54 combinations of packing

fraction and depletant size ratio showed that depletion attraction, reaching a maximum well depth of 6.8 k_B , drives reliable crystallization within 340 relaxation times above a packing fraction of 0.52, versus no crystallization within 2,000 relaxation times below 0.44 or in depletant-free controls. Entropy gain per depletant particle rose from 1.9 to 3.4 k_B as size ratio increased from 0.10 to 0.30, and crystallite domain size at the highest packing fraction tested was 2.6-fold larger than at a modestly lower packing fraction. These findings establish depletant size ratio and total packing fraction as largely separable design levers for engineering the strength, kinetics, and final structure of purely entropy-driven colloidal self-assembly.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

B.H. conceived the study, designed the simulation parameter grid, and led the writing of the manuscript. O.M. implemented the Brownian dynamics code and depletion-potential calculations. R.K. performed the crystallization and domain-size analyses and prepared the figures and tables. All authors contributed to interpretation of the results and approved the final manuscript.

Ethics Statement

This study involved no human or animal subjects and required no ethics committee approval.

Data Availability

The Brownian dynamics simulation code, parameter files, and processed crystallization and domain-size datasets supporting the findings of this study are available from the corresponding author on reasonable request.

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