Journal of Colloid and Interface Science 449 (2015) 270–278

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Modeling depletion mediated colloidal assembly on topographical patterns

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ARTICLE INFO

Article history:
Received 1 November 2014
Accepted 1 December 2014
Available online 6 December 2014

Keywords:
Tunable depletion attraction
Patterned excluded volume
Reconfigurable colloidal assembly
Monte Carlo simulations
Non-close packed structures

ABSTRACT

This work reports a model and Monte Carlo simulations of excluded volume mediated interactions between colloids and topographically patterned substrates in the presence of thermosensitive depletants. The model is matched to experiments to yield density, free energy, and potential energy landscapes that quantitatively capture particle microstructures varying from immobilized non-close packed configurations to random fluid states. A numerical model of local excluded volume affects is developed to enable computation of local depletion attraction in the presence of arbitrary geometries. Our findings demonstrate a quantitative modeling method to interpret and predict how surface patterns mediate local depletion interactions, which enables the design of colloidal based materials and devices.

1. Introduction

Depletion interactions arise between colloids and surfaces from “solute particles” being depleted, or excluded, from the gap between interacting objects [1]. When this occurs, pure solvent in the excluded volume has a different chemical potential from the solution outside the excluded volume. This produces an attraction between particles and surfaces proportional to the product of osmotic pressure and the excluded volume. Although depletion potentials become more complicated based on how solute particles interact with each other and surfaces [2], the basic picture presented above qualitatively captures the mechanism of colloidal depletion attraction for diverse solutes (*e.g.*, polymers, micelles, hydrogel particles, nanoparticles [3]). Because depletion interactions can occur in any mixture when a solute is excluded between surfaces, such interactions are expected to be ubiquitous in complex industrial formulations as well as biological systems [4].

By understanding the mechanism of depletion attraction, there is an opportunity to design such potentials by either controlling the osmotic pressure or designing the excluded volume. Examples of tuning the depletant osmotic pressure have included thermosensitive micelles [5], hydrogel particles [6,7], and polymer chains [8]. However, in each of these examples, the osmotic pressure changes because the depletant size changes, which also means the excluded volume changes (which depends on relative depletant and colloid dimensions). Beyond tuning depletant dimensions, exclude volume has been manipulated via surface geometries in several key examples including confining surfaces [9,10], surface features [11], templates for crystallization [12,13], surface roughness [14,15], and lock-and-key colloids (*i.e.*, local curvature) [16]. Although such studies demonstrate clever examples of tuning depletion interactions to affect colloidal assembly, accurate models have not been sufficiently developed to allow for systematic design and control of surface geometries that mediate local depletion potentials in colloidal materials and devices.

Here we report the development of a new method to compute local excluded volume and depletion interactions between particles and physically patterned surfaces. This method is used to analyze measurements of temperature dependent particle configurations on microfabricated surface topographies in the presence of thermosensitive depletants. Specifically, we analyze particles interacting with arrays of circles with sloping walls that produce additional local excluded volume (left side of Fig. 1, experiments reported elsewhere [17]). These measurements, and the new model reported here, are distinct from our prior study of patterned depletion mediated colloidal crystallization on an underlying gravitational energy landscape [7]. The present work is both scientifically and technologically novel by exploiting local excluded volume effects in conjunction with thermosensitive depletants to create non-close-packed reconfigurable structures. Such non-close-packed structures with length scales comparable to electromagnetic radiation have important applications as metamaterials and their reconfigurability can allow such systems to be used as static materials or programmable devices [18]. Ultimately, our findings demonstrate a quantitative modeling tool to

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http://dx.doi.org/10.1016/j.jcis.2014.12.002

interpret and predict how local surface geometries alter local depletion interactions, which can enable new colloidal based materials and devices.

2. Theory

2.1. Net interaction potential

The net potential energy for colloidal particles interacting with each other, an underlying surface, and gravity (see Fig. 2) can be modeled as the superposition of independent potentials. For a charged colloidal particle i with radius, a, in the presence of non-adsorbing depletant particles, the net interaction potential is given by,

$$u_i(\mathbf{r}_i) = u_D^{pw}(\mathbf{r}_i) + u_E^{pw}(\mathbf{r}_i) + u_G^{pf}(z_i) + \sum_{j\neq i}\left[u_D^{pp}(r_{ij}) + u_E^{pp}(r_{ij})\right] \qquad (1)$$

where $\mathbf{r}_i = (x_i, y_i, z_i)$ is position vector of particle i, z_i is the particle center-to-surface elevation relative to the underlying surface, and r_{ij} is center-to-center separation between particles i and j. Subscripts refer to: (E) electrostatic, (G) gravitational, and (D) depletion, and superscripts refer to: (pp) particle–particle, (pw) particle–wall, and (pf) particle–field. The range of electrostatic repulsion in this work is sufficient so that van der Waals interactions van be neglected.

2.2. Gravitational potential

The gravitational potential energy of each particle depends on its elevation above the reference surface multiplied by its buoyant weight, G, given by,

$$u_G^{pf}(z) = Gz = (4/3)\pi a^3(\rho_p - \rho_f)gz \qquad (2)$$

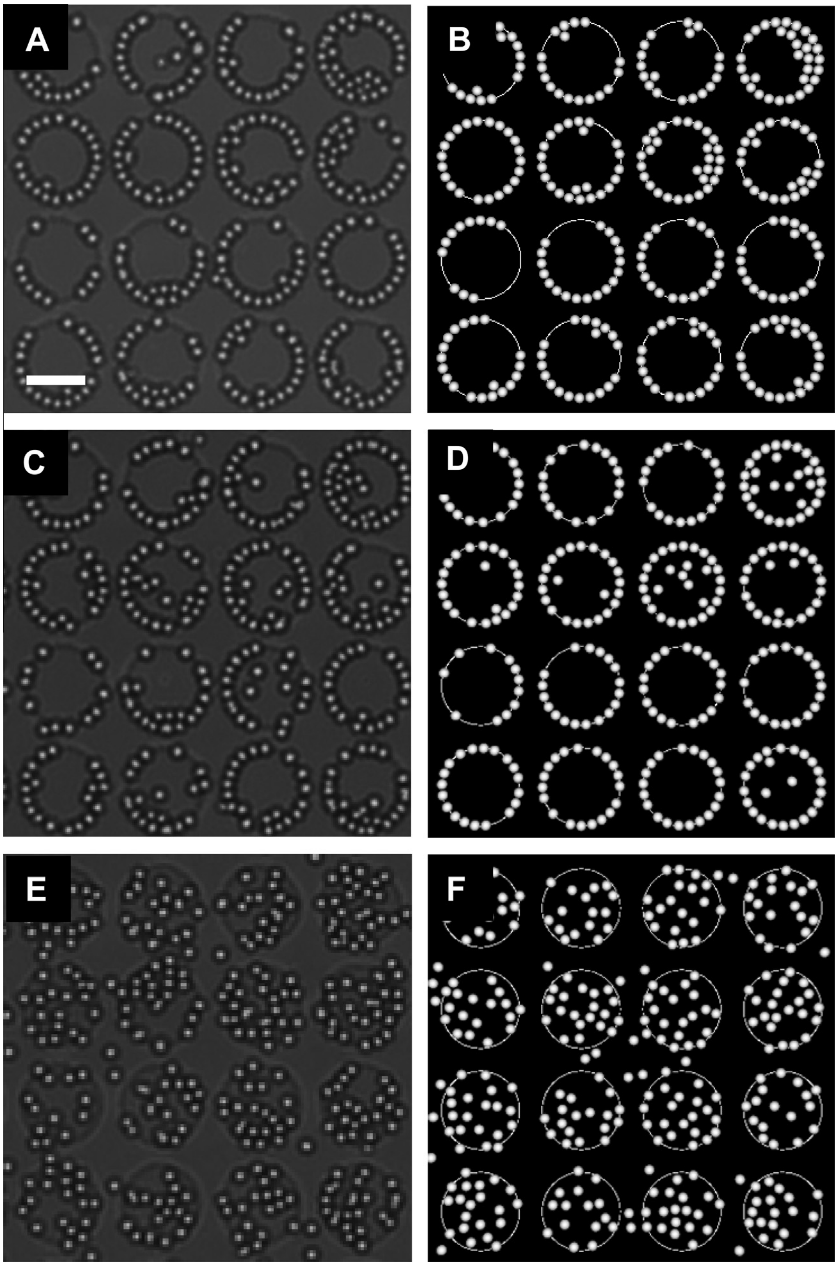

Fig. 1. Experimental images (A, C, E) and simulation renderings (B, D, F) of charged ~2 μm SiO_2 colloids at 0.18 area fraction experiencing depletion attraction with each other and a topographically patterned (well depth H = 285 nm) glass microscope slide surface. The depletion potential is tuned by the depletant size, $2L$, at 25 °C, $2L$ = 113 nm (A, B), 35 °C, $2L$ = 107 nm (C, D), 37 °C, $2L$ = 53 nm (E, F).