



# Self-assembly of artificially manufactured microcomponents using the entropic effect



U. Okabe, T. Okano, H. Suzuki\*

Faculty of Science and Engineering, Chuo University, Japan

## ARTICLE INFO

### Article history:

Received 26 April 2016

Received in revised form 6 November 2016

Accepted 21 November 2016

Available online 30 November 2016

### Keywords:

Self-assembly

Excluded volume effect

Depletion attraction

Shape-dependent bond formation

## ABSTRACT

The excluded volume effect, or depletion attraction, is the phenomenon describing induced aggregation of colloidal particles suspended in a densely crowded macromolecule solution. In this work, we attempted to utilize this effect for the self-assembly of artificially manufactured microcomponents on a 10–100  $\mu\text{m}$  scale. The bonding energy does not originate from the nature of the surfaces, but is generated by an increase of the translational entropy of macromolecules in solution. Thus, simple immersion of the microcomponents in the macromolecule solution allowed us to observe their assembly, based on shape complementarity, to minimize the free energy of the system. However, it became apparent that elaborate design is required for specific bonding between complementary shapes, in addition to merely increasing the contact surface area.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Engineered self-assembly has been one of the major challenges in the field of microfabrication, since it is expected to enable massively parallel manufacturing of heterogeneous parts on the milli-, micro-, and nanoscale [1–6]. Although self-assembly of molecules on the nanoscale involves various combinations of non-covalent interactions and molecular recognition [7], the choice of the bonding force for the self-assembly of micromachined parts is limited. In previous studies, capillary forces (e.g., forces arising at the menisci of media [8–12]), hydrophilic/hydrophobic interactions [13,14], adhesives [15–17], and low melting point metals [18–22] have been dominantly used for bonding, due to their relatively large bonding forces on a small scale. Self-assembly of microfabricated components has been also demonstrated using magnetic [23–27] and electrostatic [28–30] forces. The above-mentioned examples are all specific to the materials used. For instance, the magnitude of capillary forces depends on the surface energy of the materials, which is controlled mainly by surface modification techniques (e.g., surface oxidation [11,31], SAM [13,32–34], and DNA mediation [35,36]). Magnetic and electrostatic assembly methods require materials with specific magnetic/electronic properties. Although these approaches are promising in many applications, there are still

cases where specific materials or surface modifications are incompatible with the functions expected for the assembled structures.

It is well known in biological and colloidal sciences that a force independent of material properties can arise and even become dominant in a crowded environment, i.e., the attractive force termed ‘excluded volume effect’ or ‘depletion attraction’ has a purely entropic origin. Since entropy is only related to the spatial arrangement of molecules or objects, this force is independent of the surface chemistry and bulk properties. In molecular biology, it is thought that the ordered supramolecular structures found in cells (protein complexes, packed structures of nucleic acids, etc.) are formed due to the crowding of the intracellular environment by ubiquitous macromolecules [37–42]. In colloidal sciences, particles in the range of sub- to several microns in diameter are reported to aggregate without chemical or surface-specific interactions in the environment crowded by background macromolecules or nanoparticles [43–46]. Recently, the same attraction force has been used to assemble asymmetric (non-spherical) colloidal particles, formed by various methods, into ordered structures [47–50].

In this work, we investigated the applicability of the excluded volume effect to the assembly of larger objects (several to tens of microns) fabricated by the Micro-Electro-Mechanical-Systems (MEMS) technology. It is a simple one-pot procedure, where the photolithographically fabricated microcomponents (6–40  $\mu\text{m}$  linear dimensions) released from the substrate are immersed into an aqueous solution containing macromolecules. We studied the conditions (i.e., the size and concentration of macromolecules) in which clustering of the microcomponents took place. On this scale,

\* Corresponding author.

E-mail address: [suzuki@mech.chuo-u.ac.jp](mailto:suzuki@mech.chuo-u.ac.jp) (H. Suzuki).

Brownian motion, the phenomenon that drives the random motion of colloidal objects on a  $<1 \mu\text{m}$  scale, was no longer effective, and mechanical agitation was necessary. Finally, we present some preliminary results of the assembly with specific bonds mediated by shape complementarity toward the assembly of highly ordered structures.

## 2. Theory

In this section, we give an overview of the excluded volume effect basic principle and our strategy to assemble artificial microcomponents. The classical hypothesis suggests that when macromolecules (or any small particles with overwhelming abundance) and other relatively large objects are both present in solution (Fig. 1a), larger objects aggregate together to reduce the volume surrounding them, which is limited by the gyration radius of macromolecules (depletion volume,  $V_{dep}$ ) (Fig. 1b) [44,51]. This transition is favored, since it increases the volume where macromolecules are able to move freely ( $V_{free} = V_{system} - V_{dep}$ ), thereby increasing the translational entropy of the system. It is similar to the familiar explanation for osmosis: water molecules in the pure solvent, which corresponds to  $V_{dep}$ , move across the semi-permeable membrane to increase the volume of the solution, which corresponds to  $V_{free}$ , which is the space available for the solute.

Thermodynamically, the entropic gain is expressed as

$$\Delta S = N_m k_B \ln \left( \frac{V_{free} + \Delta V_{dep}}{V_{free}} \right) \quad (1),$$

where  $N_m$  is the number of macromolecules in the system,  $k_B$  is the Boltzmann constant,  $V_{free}$  is the initial free volume, and  $\Delta V_{dep}$  is the change (decrease) of the depletion volume due to overlapping [51]. The corresponding free energy decrease of the system is equal to  $-T\Delta S$ , where  $T$  is the ambient temperature. Decrease of entropy due to the clustering of larger objects is neglected here, since their quantity is small compared to  $N_m$ .

When microcomponents with defined shapes are used as larger objects, they are expected to accumulate and bind at positions where the contact area is at its maximum, causing a greater decrease of  $V_{dep}$  (Fig. 2c and d). Since this bonding energy is small (not far from the thermal fluctuation energy), misaligned components with a smaller contact area can dissociate to search for the global minima (more stable bonding). The extent of bonding energy can be modulated by the size ( $\propto \Delta V_{dep}$ ) and concentration of macromolecules ( $\propto N_m$ ). Note again that the origin of this clustering does not involve any material parameters of the objects to be assembled, so that it should work for any “inert” object.

## 3. Experimental

### 3.1. Assembly of polystyrene microbeads

First, conditions leading to the onset of the depletion volume effect were examined, using  $3 \mu\text{m}$  polystyrene beads as large particles and polyethylene glycol (PEG) with various molecular weights (MW) as macromolecules. A mixture of beads (Polybead<sup>®</sup> #17134, Spherotec, 0.21%v/v at final concentration), PEG, and sodium dodecyl sulfate (SDS, 0.1 or 0.5 wt%) in water was introduced between cover glass slide spacers, separated by double-sided tape. SDS, an anionic surfactant, was included to avoid nonspecific interactions between beads or between beads and glass [45,49]. The motion of the beads was captured via an inverted microscope (Nikon Eclipse TS100) with time-lapse recording.

### 3.2. Assembly of microfabricated components

The same method was used for the assembly of microfabricated structures made of a negative photoresist. The fabrication and experimental procedure are shown in Fig. 2. A thin layer of gelatin (20 wt% v) was spun on the  $30 \times 30 \text{ mm}^2$  cover glass slide ( $\sim 1 \mu\text{m}$  thick after spin-coating at 3000 RPM) as a sacrificial layer. Then, a high aspect ratio negative photoresist (mr-DWL series, micro resist technology GmbH) was spin-coated at 3000 RPM (Fig. 2a). The pattern of the microcomponent was directly exposed using a maskless exposure system (DL-1000, Nanosystem Solutions) and was developed by the solvent (Fig. 2b).

For the initial trial,  $2 \mu\text{m}$  thick arrowhead shapes with square corners of  $6 \mu\text{m}$  width, consisting of  $2 \mu\text{m}$  short edges, were fabricated as shown in Fig. 2g and released from the glass slide as follows. First, the glass plate was heated to  $70^\circ\text{C}$ , and DI water was placed on the slide to dissolve gelatin (Fig. 2c). Subsequently, extra water was poured over the slide to rinse off the microcomponents into a test tube (Fig. 2d). After centrifugation, the supernatant was replaced by a solution containing PEG and SDS, with concentrations determined in the course of the bead assembly experiments. For the self-assembly experiment, the suspension was poured into a PDMS container ( $\sim 3 \text{ cm}$  diameter,  $\sim 5 \text{ mm}$  thickness), which was typically agitated by a rotary shaker at 120 RPM (Fig. 2f and h). Microscopy imaging was typically performed every 30 min using an inverted optical microscope (Nikon Eclipse TS100). According to this procedure, approximately one million microcomponents were introduced in the  $1.4 \times 10^3 \text{ mm}^2$  bottom area (13.5 parts/ $100 \mu\text{m}^2$ ) of the container.

The assembly of complementary shapes (lock-and-key structure) was also tested to understand the appropriate design rules for specific bonding. For this purpose, five pairs of lock-and-key shapes (10 different components, shown in Fig. 6) with a size of  $40 \times 20$  (or  $28 \times 10 \mu\text{m}$ ) were designed. In this and the following experiments, the microcomponent suspension in the above-mentioned PDMS container was agitated by a miniature magnetic stirrer bar (Fig. 2h), typically at 500 RPM. Based on the microscopic images obtained at random locations, the number of “correct” or “designed” bonds were determined and compared with that of the “erroneous” or “unexpected” bonds. Finally, the assembly of a guitar-shaped structure consisting of five components with five complementary patterns was tested, as illustrated in Fig. 9.

## 4. Results and discussion

### 4.1. Assembly of polystyrene microbeads

In previous studies of the depletion attraction, colloidal beads less than  $1 \mu\text{m}$  in size were mainly used [44,45,47,48]. Herein, we tested conditions in which components greater than  $1 \mu\text{m}$  in size assemble. Some selected images of the  $3 \mu\text{m}$  beads on the glass slide are shown in Fig. 3. Since the specific density of polystyrene ( $\sim 1.05$ ) is slightly larger than that of water, all beads settled on the glass slide within  $\sim 30 \text{ min}$ , jiggling in the 2D plane in the presence of 0.1 or 0.5 wt% SDS due to Brownian motion. Note that in absence of SDS, the beads were attached to the glass surface, and no motion was observed.

In absence of PEG, beads remained dispersed even after 12 h (Fig. 3a–b). The tested conditions and the results obtained with the PEG solution are listed in Table 1. When PEG with an average MW of less than 500 kDa was used, clustering was not observed, even at the limit of PEG solubility ( $\sim 10 \text{ mg/mL}$ ). However, when a 2000 kDa PEG was used at concentrations above  $0.5 \mu\text{M}$  (1 mg/mL), the beads that encountered each other during Brownian motion remained attached, gradually forming clusters. At this concentra-

Download English Version:

<https://daneshyari.com/en/article/5008332>

Download Persian Version:

<https://daneshyari.com/article/5008332>

[Daneshyari.com](https://daneshyari.com)