Capillary assembly of colloidal particles on patterned surfaces

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Abstract
Capillary attraction at the meniscus between tiny objects plays a crucial role in self-assembly processes. The shape of the meniscus governed by the Laplace equation devotes to a long-range attraction distinct to the DLVO defined forces. Rather than considering trapped particles on ideal smooth surfaces, we use patterned substrates with ordered nano-arrays for theoretical modeling toward the capillary assembly. The vertical elevation of particles is found to change the shape of the meniscus between particles, therefore the interaction energy and capillary force. A minimal model is developed to determine the capillary force between particles and thus the motility of particles, therefore the criterion of the crystallization of colloidal particles. It turns out that the formation of a colloidal crystal or amorphous medium depends on the optimization between the scaled particle separation by its size and the geometrical design of the supporting nano-arrays. Finally, we experimentally confirmed the capillary assembly from colloidal suspensions, by playing the control parameters defined in our theoretical model, with a nice agreement. This model system can mimic the practical applications of nano-structure fabrication on versatile real surfaces for functionality purposes.

1. Introduction

Colloidal assembly is one of important routes to manufacture products with great diversities and functionalities in various applications, such as photonic crystals [1, 2], soft lithography templates [3], and anti-reflection film [4]. There are ways of acquiring desired structures by colloidal assembly based on electrical controlling [5], optical trapping [6], capillarity [7], and chemical modification [8]. The final macroscopic structures assembled from colloidal particles by these methods greatly depends on the dynamic driving forces. In practical processes, colloids as tiny units are usually dispersed in solutions and are arranged into the ordered structures from their fluid environment. Capillary force therefore is inevitable when interfaces bridge the colloidal particles or particle–liquid boundary is exposed to the vapor phase. Taking advantage of topological tailor of the long-distance interaction in tiny particle system, the means of capillary assembly from the colloidal suspensions tuned by the solvent evaporation is economic thus widely used to access well-defined structures [9, 10]. For colloidal suspensions, DLVO (Derjaguin–Landau–Verwey–Overbeek) theory is widely accepted to describe the multiple forces among particles within complex fluids [11]. In this classic theory, apart from the straightforward electrostatic interaction due to charging, van der Waals force acts between all particles, as a dispersion force. However, the capillary assembly is fundamentally dependent on the interaction between particles in solutions with the origin of surface tension, which occurs between particles even up to hundreds micrometers away [12, 13]. Exploiting the capillary force, evaporation for example, provides the facial protocol to prepare organized films, coatings, nano-structured patterns [14–20]. As the driven force, the drying process changes the interaction among particles and brings the complexity to final structures. In recent years, sophisticated composite structures such as SLIPS (slippery liquid-infused porous surfaces) have been designed for self-cleaning by anti-deposit of pollutants [21, 22]. With consuming and evaporating of infused liquid,
dispersed particles, i.e. contaminations, on patterned substrates immersed in infused liquid aggregate due to capillary force. Once pollutants are aggregated, it is rather difficult to remove thus strongly affects the performance and reutilization of the SLIPS.

To theoretically understand the basic attraction tuned by capillary forces between particles due to the formation of meniscus, the successful model dates back to Nicolson [23]. Nicolson used bubbles floated on air–liquid interfaces to constitute a simplified model system, and derived elegantly an analytical expression of the capillary force between two particles. Kralchevsky et al [12, 24, 25] took the similar problem and derived the implicit expressions of the meniscus profile in two cases (cylinders and spherical particles). The simplification is achieved by linearizing the Laplace equation for the particles far apart. Through Green function theorem, the final shape of the meniscus is determined dependent on a line integral over three phases contact lines rather than a volume or surface integral. Consequently, the interaction energy and force were successfully calculated, which was also in good agreement with experiments [13, 26, 27]. In the recent decades, for the purpose of miniaturization, the fabrication of micro- and nano-structures with ultra-fine building blocks is highly demanding in modern industry. Therefore, versatile surfaces with considerable physical and chemical heterogeneities need to be either protected or decorated with nano-structures for functional properties, such as plasmonic enhancement [28], anti-reflection [4], wettability tuning [29], dental implants [30]. With the capillary assembly, unique micro- and nano-structures are possible to reach these massive needs. Synthetic materials and techniques down to the nano-scale have been greatly developed now called nano-science and nano-technology. Then it is intriguing to explore the controlled capillary self-assembly of colloidal particles on nano-structured substrates. Xia et al started the self-assembly of colloidal particles on patterned substrates very earlier, and successfully controlled the packing of multi-sized colloidal spheres on templates by controlled experiments [31]. Since then configurations with sufficient fancy and up to device level based on colloidal capillary self-assembly, on variety of structured substrates, have been realized, meanwhile the dependence of the final structures on numerous experimental parameters were nicely tested and quantitatively measured [9, 32–34]. These empirical relations are useful to understand and control the assembled structures by using the capillarity, on real devices and surfaces with preliminary structures instead of ideal flat substrates.

However, the capillary force for particles on real templated surfaces, still need to be specified, particularly from theoretical point of view. Since the micro- and nano-structures beneath the particles change significantly the interaction energy, considering the fact that the vertical elevation of the particle is accompanied with the horizontal motion in the evolving particle system. Hence, we here develop a minimal model to determine the shape of meniscus across the particles sitting on the nano-arrays, and calculate the interaction energy between colloidal particles on a periodical pillars. Based on this model, we can predict the motility of colloidal particles on patterned substrates during evaporation, as varying the size and separation of particles, as well as the spacing of periodical pillars. To testify the theoretical predictions on the criterion of crystallization with matching all the parameters included, we experimentally assemble polystyrene microspheres into the 2D crystals on the ZnO nano-wire array by a natural evaporation process. Parameters defined as the motile probability and crystallization degree for polystyrene beads, are quantitatively measured. We achieve a nice agreement between the theoretical prediction and experimental results. This model and demonstration of crystallization process from colloidal particles can help us understand the capillary assembly, as well as provide practical clues to match the particle size with patterned structure dimension. As a consequence, either colloidal crystal or amorphous medium can be realized in a controllable way.

2. Methods and materials

2.1. Mathematical model

In fact, capillary assembly of colloidal particles contains rich and complicated dynamics due to the coupling between geometric structures on surface, particle concentrations as well as evaporation process. For simplification, we assume that the substrate is hydrophilic leading to a covered thin liquid layer. Hence, the decreasing of liquid layer due to evaporation is regarded to be homogeneous and thus convection caused transporting is neglected. The initial dilute colloidal suspension allows particles to be separated and we only considered the course before jamming happened. We also suppose the patterned surfaces to be uniform nano-pillars with constant spacing, differing from ideal smooth substrates. Bring this new geometry totally changes the landscape of interaction energy of the system. The motile particles tending to crystallization, are dragged out of the initial state trapped inside the valley of nano-pillars, leading to the coupling between transverse displacements and vertical elevation as well as a distinct meniscus shape. Therefore, the remaining key task is to determine the interaction energy and capillary force between particles, which is equal to find the detailed profile of the meniscus between particles. Inspired by the beautiful Kralchevsky’s
model of capillary interaction between particles on flat substrates [12], a general expression of the interaction energy between particles on patterned surface surrounded with a thin liquid layer is derived here.

Considering two particles are located on nano-structures with a distance of 2s, attaching to a liquid–fluid interface as depicted in figure 1. The nano-structures are modeled as slender pillars with a constant spacing of d. We suppose that the capillary meniscus forces would drive particles from the state that particles are trapped in pillars to the state that particles are located on the top of the pillars. The interaction energy $\Delta W$ between two particles of the considered states is defined as below,

$$\Delta W = W(s - d/2) - W(s)$$

(1)

Here, $W(s)$ is the free energy of the system that two particles have a distance of 2s. A negative $\Delta W$ represents an attraction between the two particles. The free energy of the system in both states contains four major components as shown in the following equation,

$$W = \sum_{K=1}^{2} m_K g z_K^c + \sum_{Y=I,II} m_Y g Z_Y^c + \sum_{K=1}^{2} \sum_{Y=I,II} \omega_{KY} A_{KY} + \gamma \Delta A$$

(2)

where the first two items are the gravitational potential energy of particles and fluids, the latter two items are surface energy of particle–fluids and fluids–fluids interfaces. Among, $m_K$ and $z_K^c$ is the mass and mass center of the $K$th particle, $K = 1, 2, \ldots, N$; $m_Y$ and $Z_Y^c$ is the mass and mass center of the $Y$th fluid phase and $h_k$ is the height of the $K$th particle, $K = 1, 2, \ldots, N$. $A_{KY}$ and $\omega_{KY}$ is the area and interface energy of the boundary between $K$th particle and $Y$th fluid. $\Delta A$ is the area difference between the meniscus and the xOy plane; $\gamma$ is the interface energy between two phases of fluids. The key problem of deriving the free energy of the system is to determine the meniscus profile $\zeta(x, y)$, which should satisfy Laplace equation of the capillarity [35]. Fortunately, a theoretical analysis of meniscus profile $\zeta(x, y)$ of two cylinders through an interface of two phase fluids can be borrowed [12]. We can set $z_1, z_2$ respectively to be the z limitation of the system, which will be eliminated later in the calculation as showed in figure 2.

As mentioned above, the particles are supposed to be dragged onto the top of the nano-pillars from the gaps, resulting in an increase of the mass center $\Delta z = R - \sqrt{R^2 - d^2/4}$, which can be derived directly form geometric calculation. Taking into account this rise of mass centers of particles, we can deduce a general expression of the interaction energy between two particles by simplifying the items of free energy in
The fourth item in the equation (2) is the gravity energy of the two kinds of fluid, which expressed as,

$$W_2 = \sum_{Y=I,II} m_Y g Z_Y = \sum_{Y=I,II} \rho_Y g \int_V z \, dV$$

(4)

Therefore,

$$\int_{V_1} z \, dV = \int_{xOy} \int_{y_1}^0 z \, dz \, dy - \int_{V_3} z \, dV + \int_{V_m} z \, dV - \int_{V_1} z \, dV$$

(5)

$$\int_{V_{II}} z \, dV = \int_{xOy} \int_{y_2}^0 z \, dz \, dy - \int_{V_m} z \, dV - \int_{V_2} z \, dV$$

(6)

Here $V_m$ is the volume between meniscus profile and its projection on $xOy$ plane, $V_1$ is the overlapped volume between $V_m$ and spheres, $V_3$ is the volume of spheres beneath $x$ axis, $V_2$ is the volume of spheres excepting $V_1$ and $V_3$. Both of them are showed by different graphic patterns in figure 2. The difference of the gravity energy of the two kinds of fluids denoted by $\Delta W_2$ is expressed as,

$$\Delta W_2 = \rho ( \int_{V_1} z \, dV - \int_{V_m} z \, dV ) + \rho ( \int_{V_2} z \, dV + \int_{V_m} z \, dV )$$

(7)

$$\Delta W_2 = \Delta \rho \left( \int_{V_m} z \, dV - \int_{V_{II}} z \, dV \right)$$

(8)

The third item in the equation (2) is the interface energy between particles and two kinds of fluids. The energy at initial and subsequent state are as following respectively,

$$W_3(s) = 2 \times \{ \omega_I \cdot f(h_c + l_0 + \Delta z) + \omega_{II} \cdot f(2R - h_c - l_0 - \Delta z) \}$$

(9)

$$W_3(s - \Delta h/2) = 2 \times \{ \omega_I \cdot f(h_c' + l_0) + \omega_{II} \cdot f(2R - h_c' - l_0) \}$$

(10)

where $f(h) = 2\pi Rh$ is the surface area of a spherical cap with height $h$. The particle fluid interface energy difference reads

$$\Delta W_3 = 4\pi R (\omega_I - \omega_{II})(h_c' - h_c - \Delta z)$$

(11)

The fourth item in the equation (2) is the surface energy of two kinds of fluids, which is given by,

$$W_4 = \gamma \Delta A = \gamma (\Delta A_p - 2\pi r^2)$$

(12)

where $\Delta A$ is the area difference between meniscus surface and the $xOy$ plane in the system. $\Delta A_p$ is the area difference between meniscus surface and its projection on $xOy$ plane. When the slope of the meniscus surface is small, i.e., $\xi_{xx} \ll 1$ and $\xi_{yy} \ll 1$, the expression of $\Delta A_p$ can be derive through solving Young–Laplace equation of contact lines in bipolar coordinates [12], which is

$$\Delta A_p = 2\pi r c \sin \varphi - \Delta \rho \int_{V_m} z \, dV$$

(13)
The projection of contact line on xOy plane can be approximately to be a circle with radius of $r_c$. $h_c$ is the average height of contact lines of three phases, $\Psi_c$ is the angle between horizontal and the tangential of contact lines. Therefore, the fourth item of equation (2) can be transformed to,

$$\Delta W_4 = 2\pi \gamma (r_c' h_c' \sin \Psi_c' - r_c h_c \sin \Psi_c - r_c^2 + r_c') - \Delta \rho g \left( \int_{V_m} z \, dV - \int_{V_m} z' \, dV \right)$$  \hspace{1cm} (14)

It is clearly that the latter term of this $\Delta W_4$ is exact the equation (8). Thus, to combine equations (3), (8), (11) and (14), the interaction energy can be given by,

$$\Delta W = -4\pi \gamma R \cos \theta (h_c' - h_c - \Delta z) + 2\pi \gamma (r_c' h_c' \sin \Psi_c' - r_c h_c \sin \Psi_c - r_c^2 + r_c')$$  \hspace{1cm} (15)

The equation (15) is the main and final formula of the interaction energy. Note that the term of equation (3) is omitted here since it turns out to be negligible based on our numerical calculation. Additionally, $\omega_1 - \omega_2 = -\gamma \cos \theta$, considering equilibrium contact line without contact angle hysteresis. To obtain the value of related parameters in equation (15), a nonlinear equation set from geometric consideration needs to be solved. Suppose $l$ is the average distance between contact line and the bottom of the particles, then we have $l = h_c + l_0 + \Delta z$. Here, $l_0$ is the thickness of phase I fluid layer, which is fixed to be 50 mm in our calculations, simulating the end of the evaporation process.

Obviously, in order to use the governing formula equation (15), we need the transferring parameters and items $r_c(l)$, $\Psi_c(l)$, $a(l)$, $\tau_1(l)$ and $h_c(l)$. The projection radius of the contact line is $r_c(l) = \sqrt{2R - l}$. Depending on the wetting properties, the angle between the meniscus at the contact line and x-axis is $\Psi_c(l) = \arcsin(r_c(l)/R) - \theta$. From the sketch of figure 2, the geometrical relation gives $a(l) = \sqrt{s^2 - r_c^2(l)}$, and the variable in bipolar coordinates has the form of $\tau_1(l) = \ln(a(l)/r_c(l)) + \sqrt{1 + a^2(l)/r_c(l)^2}$. Also, the mean height of the contact line on the particles is defined as $h_c(l) = r_c(l) \sin \Psi_c(l) \{\tau_1(l) + 2 \ln(1 - e^{-2\pi/(\tau_1(l))})/\tau_1(l)\}$. In the present case, $\gamma_c = 1.78$ and $\ln(\gamma_e$ is Euler–Mascheroni constant, $\gamma = 1/\sqrt{2\Delta \rho g / \gamma}$ is the capillary length, with a value of 2.7 mm here. Note that as $\Delta z$ approaching to zero, the current model degrades into the case for flat substrates. At this stage, this nonlinear equation set is closed and can be solved numerically by self-written Mathematica code.

2.2. Experiments

Zinc oxide nano-wire arrays (ZnO NWs) is synthesized from an aqueous growth solution by a two-step process. In brief, the glass substrates are coated with a ZnO seed layer by a sol–gel technique. The precursor solution is prepared by dissolving equimolar (0.75 M) zinc acetate (Zn(CH3COO)2: 2H2O) and diethanolamine (C2H8N2O) in ethanol. After spin-coated on the clean glass substrates, the wet films are annealed at 380°C for 20 min. Subsequently, ZnO NWs were synthesized in alkaline aqueous solution of equimolar (0.05 M) zinc nitrate Zn(NO3)2 · 6H2O and hexamethylenetetramine (CH2)6N4 with the seeded substrates up-side down at 90°C for 6 h. All of the resultant nano-wire arrays are rinsed with de-ionized (DI) water. In order to remove the residues of growth solution on the surface of the samples completely, all samples are immersed into the de-ionized water for 24 h, and then dried with the dry N2 flux. The average diameter and height of ZnO nano-wires are about 150 nm and 7 µm, respectively.

The aqueous suspensions of polystyrene microspheres (PS, purchased from Huake Micro-tech, China), have radius of 385 nm, 695 nm and 1565 nm, respectively. The distances between particles on substrates are controlled by adjusting the concentrations of particle suspensions. Concentrations, 0.1% wt and 0.5% wt, are used to demonstrate the movement and crystallization of particles under capillary forces, respectively. The same volume (5 µl) of PS microsphere suspensions are transferred onto the ZnO NWAs. The experimental process is explained by the cartoon in figure 3. The optical microscope was employed to record
the position changes of PS microspheres during evaporation and the evolution of the morphology of 2D particle films after drying. The image data of the microscope were processed by ImageJ (NIH open source software) to determine the microspheres which have moved during the evaporation process and to distinguish the crystallization degree of the 2D particle films. The scanning electron microscope (SEM, FEI QUANTA FEG 250) was used to show some details of the microsphere deposits, such as the distance between the microspheres and the positional relationship between the spheres and the nano-wires.

3. Results and discussion

3.1. Phase diagram

Intuitively, the bigger particles move easier on nano-array with high density of the pillars (i.e. small spacing $d$, the extreme case is a flat carpet). Similarly, the high number density of particles, corresponding to a small distance between particles $s$, suppresses the pinning of particles sitting in pillar valleys. Therefore, the two distance parameters $d$ and $s$ establish a phase diagram to predict the moving or pinning behaviors of particles. The phase diagrams of the motility of particles with different radius corresponding to experimental conditions are showed in figure 4. By using the equation (15), the interaction energy between particles $\Delta W$ can be numerically solved.

For particles with a given radius, as varying the scaled separation between two spheres $s/R$ and the array spacing $d$, the light blue regime represents a negative interaction energy $\Delta W$ thus an approaching of the neighbor particles in consequence. Thus, if the number densities of the particles and nano-pillars are set within this blue region, it is highly possible to assemble the particles into a closed ordered layer or uniform 3D crystal on this patterned substrates. In contrast, gray regime represents a positive interaction energy $\Delta W$ therefore a pinning behavior of particles, which indicates the crystal phase of the particles is less favorable, particularly 2D colloidal crystal is impossible. For all the cases with different particle radius, there are always two regions distinguishing the moving or pinning of particles. Bigger particles have high possibility to crystallize, which can be quantitatively discussed by defining a motion probability $\sigma$ as the following section.

3.2. Motion probability of particles

In reality, both the nano-arrays on substrates and the particle separations present heterogeneity as shown in figures 5(a)–(g). To take this into account, we introduce normal distributions both in nano-arrays spacing and particle separations. The spacing of the nano-arrays has a mean value of 150 nm with a standard deviation of 150 nm, measured through SEM figures. The particle separation is approximately of $s = 3 \pm 0.2R$, measured by optical microscopy. The average spacing is calculated through the ratio between considered area and particle amount. Here we define a numerical parameter $\sigma$ to be the ratio between the moved particle number and the total particle number. Basically, we can first correspond the moving and pinning state to a numerical value unit and zero respectively. For a specific distribution of pillar spacing $d$, we can get an effective move ratio at a given particle separation $s/R$. These effective move ratios then can be weighted by another given distribution of particle separation, eliciting to the numerical parameter $\sigma$ defined above. The theoretical calculation is plotted with dashed line in figure 5(h) shows the dependence of the motion probability of particles on their radius.

In order to make the comparison between the theoretical results and experiments, we carefully checked the evolution of paritcles on nano-rrays driven by the evaporation with dynamical fluctuation of the
Figure 5. Snapshots of the particle evolution and distribution on the nano-structured substrates, and the motion probability of particles depending on their size. (a)–(c) These are typical optical snapshots of colloidal particles ($R = 1565$ nm) on ZnO nano-array. The particles in the red circles are the moved ones. (d)–(f) SEM snapshots of the colloidal self-assembly on ZnO NW A from colloidal particles with radius of 385 nm, 695 nm, and 1565 nm respectively. (g) The ratio of motile particles $\sigma$ of different radius $R$, comparing experimental measurements and theoretical calculation.

meniscus across the particles. Figures 5(a) and (b) shows the snapshots of PS microspheres on ZnO NWA before and after dried respectively. The moving particles can be easily detected by the mismatch between red and green marked particles in the overlapped image as shown in figure 5(c). As shown in figure 5(h), theoretical calculation of the motion probability $\sigma$ get a quantitative agreement with experimental results. Although there is a slight deviation between theory and experiments, the general tendency of $\sigma$ with $R$ is roughly the same. This deviation could be reasonably caused by the dispersity of particle size and non-uniform ZnO NWA height, as shown in figure 5(g).

In addition, we employed the SEM to get further information of dried samples as shown in figures 5(d)–(f). There is a significant phenomenon that the larger particles they are, the more contacted particles exist. Quantitatively, the proportions, between the contacted particle number and total particle number, are around 0.46, 0.57, and 0.93, corresponding to particles with radius of 385 nm, 695 nm and 1565 nm respectively. The compact particle regime in the figures means the particles are approached to each other and less impacted by the substrates during evaporation. Eventually, we get a consistent results with optical microscopy observation and theoretical calculation.

3.3. Criterion of control parameters

There is a question that how to fabricate the proper nano-pillars to match the requirement of colloidal particles assembly. For colloidal self-assembly on nano-structured surfaces, the straightforward control parameters are the radius of particles, the concentration of colloidal suspension, and the detailed dimension of nano-structures on substrates. For practical reason, high quality functional colloidal particles and nano-structures are usually of cost concern. Thus, for a given size of particles or geometry of nano-structures, it is desirable to provide the optimal range of other control parameters aforementioned.

Besides, the concentration of colloidal suspension is related to the mean distance between colloidal particles. Meanwhile the geometry design of the nano-arrays beneath is the selection of mean spacing of the nano-pillars. To give a general criterion to guide capillary assembly of colloidal particles on structured surface, the relation of the maximum spacing of periodical pillars $d_m$, allowing particles crystallization, dependent on the scaled particle separation $s/R$ is derived from our theoretical model. As shown in figure 6, the allowed spacing of nano-pillars $d_m$ is inversely proportional to the separation of colloidal particles $s/R$. Furthermore, $d_m$ rises as the sphere radius increasing.
Here we explain how to use the theoretical calculation results plotted in figure 6 for practical applications. For example, the particle used for self-assembly has a radius of 1.2 \( \mu \)m, as denoted with green triangle symbols. If the mean distance between particles is selected as \( s/R = 9 \) (i.e. \( s \sim 10 \mu \)m, corresponding to a 2D volume fraction of 0.25), the maximum allowed spacing of nano-pillars is about 50 nm for 2D colloidal crystal. This spacing needs high resolution lithography techniques at high cost. While, if taking \( d_m \) as 100 nm, we can directly see from figure 6 that the corresponding \( s/R \) is about 3, indicating that we need particles with specific concentration for self-assembly adapting to the pattern of substrates for crystallization. Then \( s/R \) should less than 3, i.e. the higher volume concentration \( \phi \) of the colloidal solution. More accurate volume concentrations in practices can be estimated according to \( \phi = \pi R^3/[3(s + R)^2H] \), where \( H \) is the height of liquid film.

3.4. Colloidal crystals
Certainly, the pair-particles attraction considered in our model needs to assist real closed packed crystals, where there are more complicated interactions between the microspheres during capillary self-assembly process. In order to verify that whether our model is suitable for cases of high concentrations of colloidal suspensions, here we use a 0.5% wt PS suspension for a demonstration. Due to the high concentration, the optical microscopy cannot capture the detailed motion of the microspheres during the evaporation process. We instead characterize the final structures on the dried samples. For resolution reason of imaging, we avoid the multi-layered region and check the most dense single-layer region on the dried samples.

In figure 7, the first and second row are the snapshots of dried samples after evaporation self-assembly of microspheres with three different radii on ZnO NWA and glass respectively. In order to compare easily, we have enhanced contrast of the images and perform the fast Fourier transform (FFT), as shown in the insets of figure 7. From the panels in the first row, we can see that as the size of microspheres increasing, the interference fringes gradually appear and the FFT images show the regular hexagonal patterns. This implies that the larger the size of microspheres, the higher order of the self-assembled crystal on the structured substrate. Since the larger microspheres have a higher mobility on structured substrate to form higher order of self-assembly structures, which is consistent with our model. In addition, the assembled patterns of the...
same size microspheres on the glass are more ordered than that on ZnO NW A. The clear hexagonal patterns in the FFT images also show that the microspheres have more ordered self-assembled patterns on the glass, and even crystallization appear in figures 7(d) and (e). Since the glass is relatively flat, we can equivalently think that its surface is composed of ultimate dense pillars. In other words, this situation is equivalent to the spacing of the pillars approaching to zero nanometer in our model. Hence the mobility of microspheres on the glass substrate is very high, no matter what the size of the microspheres are. This recovers the results in Kralchevsky’s model [12]. To be noticed, in figure 7, the order of the self-assembled pattern of microspheres with a radius of 1565 nm on glass is significantly lower than that of smaller microspheres. This is just owing to the size heterogeneity of the PS microspheres used here is improved when the microspheres get larger.

4. Conclusion

In summary, we develop a mathematical model to describe the interaction energy between particles on patterned surfaces instead of ideal smooth surfaces. Our model uses the difference of free energy of two typical successive particles locations on periodical nano-pillars to predict the direction of capillary force. The calculation here shows that the motility of particles on nano-pillars are governed by the size and separation of the particles, and the spacing of base pillars as well. When the capillary self-assembly of colloidal particles is required on a structured substrate, our model can suggest colloidal suspension concentration, colloidal particles and structural dimensions for different applications. From our experiments, we observed the displacements of PS particles on ZnO NW A before and after evaporation through an optical microscopy. Taking into account the dispersity of particles distances and non-uniform spacing of nano-pillars beneath, the motility of particles meets a good agreements between experimental measurements and theoretical calculation. We have verified the approximate proportional relation between the moving probability and the size of spheres, by the statistics of the proportion of contacted microspheres, driven by the capillary force on the same structure. In addition, our model also provides a guidance on maximum nano-structure spacing of substrates for particles to form crystallization through capillary assembly. Finally, through the higher concentration of colloidal solution evaporation self-assembly experiments, we found that the orders of assembled microsphere patterns are increasing with the radius of microspheres. This implies that our simplified model is applicable even there are more complex inter-sphere interactions.

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