# Monte Carlo simulation of particle dynamics in bi-dispersed colloidal droplets

Pavel A. Zolotarev[1,2], Konstantin S. Kolegov[1,2,3]

[1]Astrakhan State University, 414056 Astrakhan, Russia

[2]Landau Institute for Theoretical Physics Russian Academy of Sciences, 142432 Chernogolovka, Russia

[3]Caspian Institute of Maritime and River Transport, the Branch of Volga State University of Water Transport, 414000 Astrakhan, Russia

## Abstract

Colloidal droplets are used in a variety of applications. Some of them require the presence of particles of different sizes. These include methods of medical diagnostics, the creation of photonic crystals, the formation of supraparticles, and the production of membranes for biotechnology.

Some experiments have previously shown the possibility of particle separation by their size near the contact line. We have developed a mathematical model that describes this process. Bi-dispersed colloidal droplets during their evaporation on the hydrophilic substrate with a small contact angle were taken in our consideration. In such a system, a monolayer of particles is formed near the periphery of the drop. This pattern form is associated with the effect of coffee rings. The model takes into account the transport by the flow caused by the evaporation of the liquid and the diffusion of particles.

We carried out a Monte Carlo simulation for several particle concentrations. The results of the calculations correspond to experimental observations when smaller particles accumulate closer to the contact line than relatively large particles.

## Introduction

One of the most important and actively discussed problems is connected to studying structures of colloidal particles, which emerge on the surface of an evaporating sessile droplet and remain on the substrate after drying. One of the examples is the effect of evaporative contact line deposition, the so-called coffee-ring effect. While a droplet is drying on the substrate, capillary flows carry the colloid particles toward the three-phase boundary. In this case, formation of an annular deposition is observed if the contact line was pinned throughout the entire process. Tak-Sing Wong et al. showed in their experiment that it is possible to use the coffee ring effect for particle separation by their size (Fig. 1). This is useful for a variety of applications. For example, it has direct implications for developing low-cost technologies for disease diagnostics in resource-poor environments. To understand this mechanism clearly, we employ a simplified mathematical model, which accounts for joint consideration of advection (capillary flow) and particle diffusion.

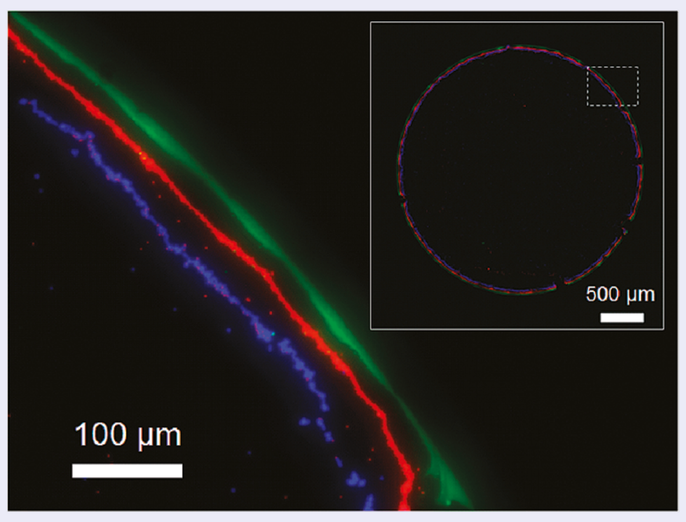


Figure 1: Optical fluorescence image showing the separation of 40 nm (green), 1 $\mu m$ (red), and 2 $\mu m$ (blue) particles after evaporation. Reproduced with permission from [Anal. Chem. **83**, 1871–1873 (2011)]. (©2011, ACS).

## Methods

Let us consider an evaporating bi-dispersed colloidal droplet on a hydrophilic substrate (Fig. 2). There are small ($r_p \approx 0.5$ $\mu$m) and large ($r_p \approx 1$ $\mu$m) particles suspended in this solution, where $r_p$ is the particle radius. The contact radius of the droplet with the substrate, $R$, is constant in time, that is, the contact line does not move (pinning). The contact angle $\theta$ is quite small, so a monolayer of particles is formed in the sediment. The approximate expression for the shape of the droplet surface is

$$h(r,t) = \theta(t)\frac{R^2 - r^2}{2R}, \qquad (1)$$

where radial coordinate is $r = \sqrt{x^2 + y^2}$. Let the fixing radius $R_f$ define a boundary, where the particle size and the local droplet height are comparable (particle diameter of $d_p = 2r_p \approx h$), provided that $R_f < R$. In a thin droplet, the particles cannot reach the contact line, because the local droplet height is very small in the vicinity of the contact line. The fixing radius depends primarily on particle size. From (1) we derive the dependence of the fixing radius on time

$$R_f(t) = \sqrt{R^2 - \frac{4r_pR}{\theta(t)}}. \qquad (2)$$

We assume that the contact angle $\theta$ decreases linearly over time since this corresponds to a variety of experiments.

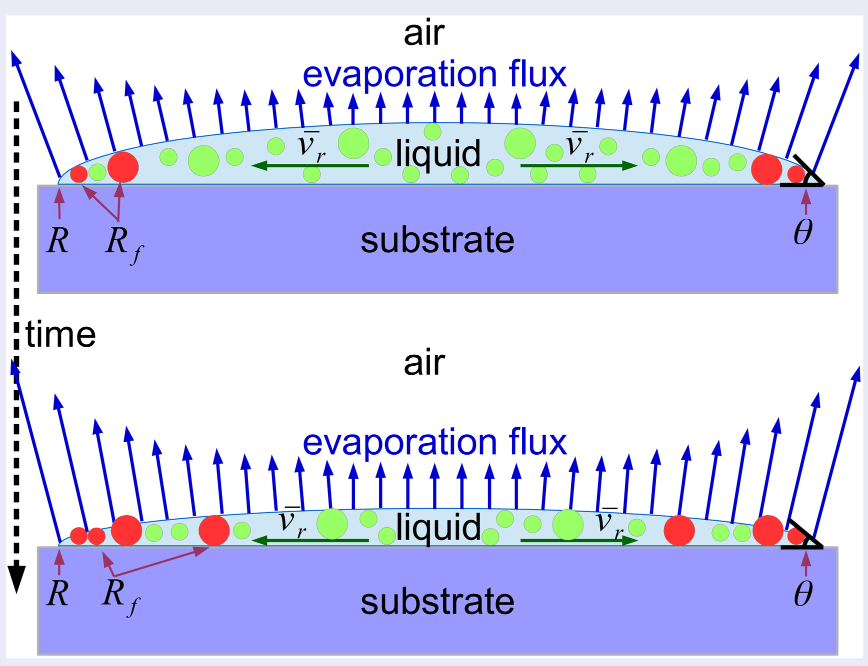


Figure 2: Sketch to the problem definition.

Height averaged radial velocity of fluid flow

$$\bar{v}_r = \frac{R}{4\tilde{r}(t_{\max} - t)}\left[\frac{1}{\sqrt{1-\tilde{r}^2}} - \left(1 - \tilde{r}^2\right)\right], \qquad (3)$$

where $\tilde{r} = r/R$. The diffusion displacement distance is $\delta l_{\mathrm{dif}} = \sqrt{2D\delta t}$. Brownian motion of the particles is simulated using a Monte Carlo method. We denote a random angle between a particle displacement and the $x$-axis as $\alpha$, $\alpha \in [-\pi;\pi)$.

Then the displacement of a particle is described by the vector $(\delta x, \delta y)^T = (\delta l_{\mathrm{dif}}\cos\alpha, \delta l_{\mathrm{dif}}\sin\alpha)^T$. The particles can be in different states during the calculation. Let us mark the moving particles by green. The particles deposited in the sediment are red. The diffusion coefficient is calculated using the Einstein formula $D = kT/(6\pi\eta r_p)$, where $k$ is the Boltzmann constant. The values of the temperature $T$ and the viscosity $\eta$ of the liquid are taken for water under normal room conditions. The value of time step $\delta t = 10^{-4}$ s was chosen on the basis of a series of computation experiments to satisfy the Einstein relation for the mean square displacement $\langle \delta L^2_{\mathrm{dif}} \rangle = 2Dt_{\max}$, where $\delta L_{\mathrm{dif}}$ is the total displacement during the period $t_{\max}$, and the averaging is performed over all particles. The algorithm of the program is as follows.

**Algorithm 1** Particle dynamics algorithm.

Problem parameters definition: $r_s$, $r_l$, $R$, $N_s$, $N_l$, $t_{\max}$.
Generation random coordinates of the particles $x_i$ and $y_i$ ($i \in [1; N_p = N_s + N_l]$).
By default, all particles are marked green.
**for** $\tau \leftarrow 1, t_{\max}/\delta t$ **do**
  calculate $R_f$ for small and large particles.
  **for** $i \leftarrow 1, N_p$ **do**
    changing the particle status if necessary.
  **end for**
  **while** (not all particles are displaced) & (there is a shift of at least one particle) **do**
    shuffle the array of particle numbers.
    **for** $i \leftarrow 1, N_p$ **do**
      red particles are skipped.
      **if** (green particle) **then**
        calculate the new particle coordinates due to diffusion.
        **if** (no collision) **then**
          move the particle.
        **end if**
        Calculate the new particle coordinates due to advection.
        **if** (no collision) **then**
          move the particle.
        **end if**
      **end if**
    **end for**
  **end while**
  Write the particle coordinates, radii, and colors to a file for the current time step.
**end for**

In the calculations, we consider three cases with different particle concentrations.

## Contacts

Konstantin S. Kolegov. Email: konstantin.kolegov@asu.edu.ru

## Further reading

[1] P. A. Zolotarev, K. S. Kolegov.
Average cluster size inside sediment left after droplet desiccation.
Journal of Physics: Conference Series. 2021. Vol. 1740. P. 012029 DOI: 10.1088/1742-6596/1740/1/012029

[2] K. S. Kolegov, L. Yu. Barash.
Joint effect of advection, diffusion, and capillary attraction on the spatial structure of particle depositions from evaporating droplets.
Physical Review E. 2019. Vol. 100, Iss. 3. P. 033304 DOI: 10.1103/physreve.100.033304

## Results and discussion

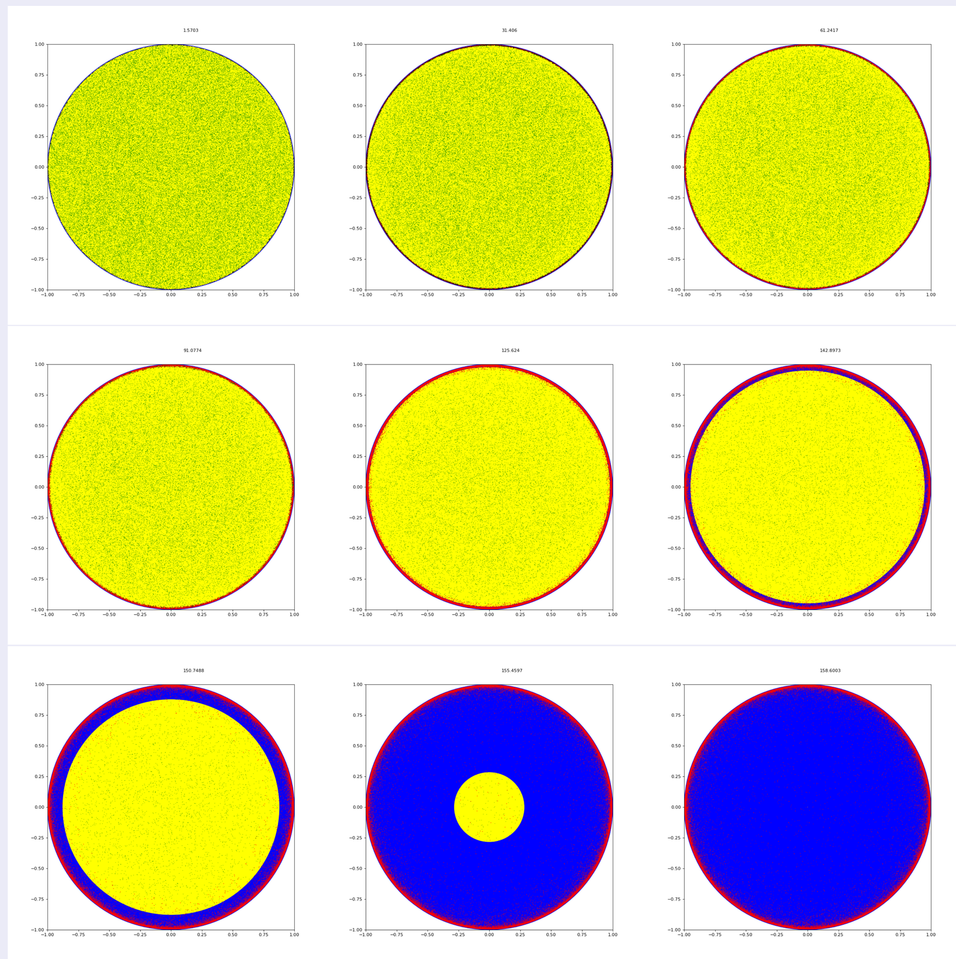

Figure 3: Screens of the calculation visualization for several time points (the time shown in the pictures is in seconds).

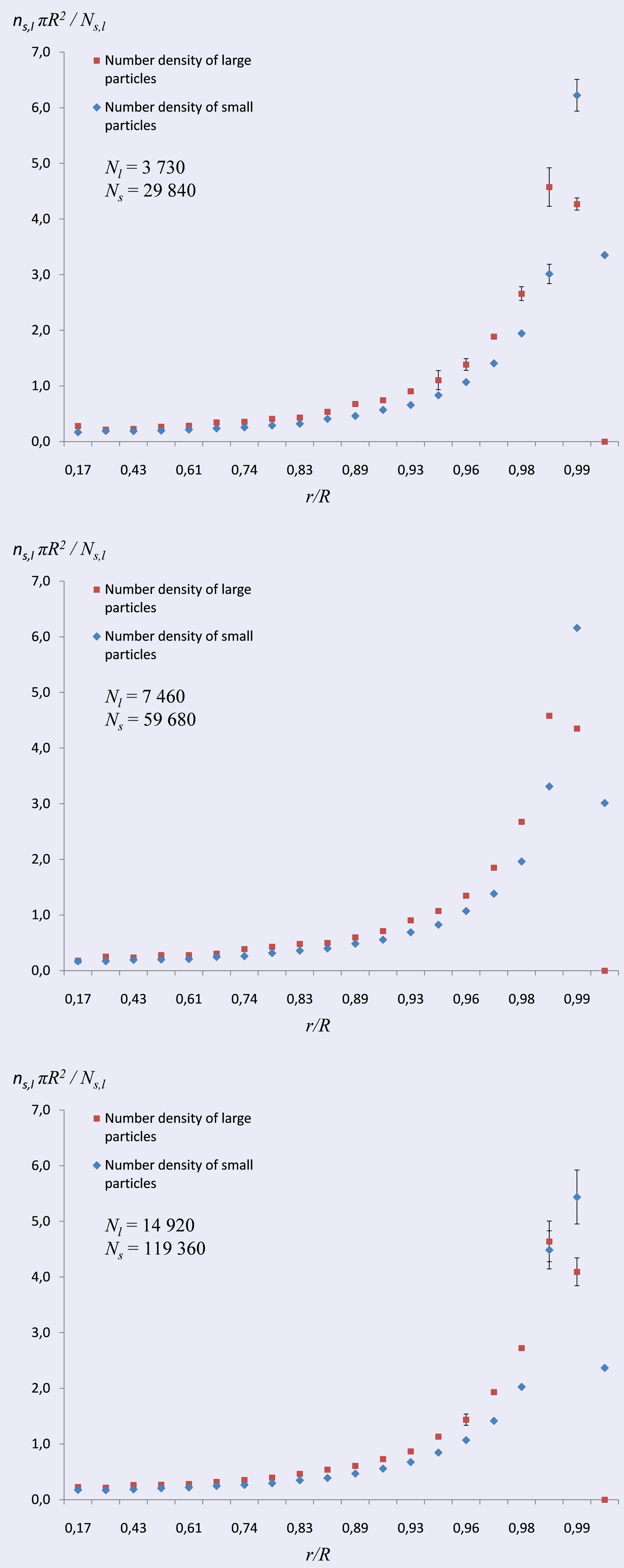


Figure 4: The scaled number density of the small and large particles is calculated for the obtained by simulation structures.

Over time, the particles are carried by the flow towards the contact line (Fig. 3). In addition, they are mixed due to diffusion, including in the area of the forming annular sediment. In the screenshots, only the position of the fixing radius for small particles is marked. The approximate location of the fixation radius for large particles can be guessed from the interspersed red dots among the green ones. It is smaller than the fixing radius for small particles. The number of particles in the sediment per unit area (number density, $n_{s,l} = N_{s,l}/S_{\mathrm{ring}}$, where $N_{s,l}$ is the small (large) particle number and $S_{\mathrm{ring}}$ is a ring square) was calculated for three cases at different solution concentrations (Fig. 4). These results indicate that a larger number of particles are located on the periphery of the dried drop. Moreover, at a small distance from the contact line, there are small particles and a little further a mixture of large and small ones. This can be observed on enlarged local areas of sediment near the contact line marked in black (Fig. 5). Clusters of particles or their mixtures are formed in the sediment at a high initial concentration of the solution. Small free spaces are visible between mixed clusters and clusters of small particles. In the case of a small number of particles, such clusters are either small or non-existent.

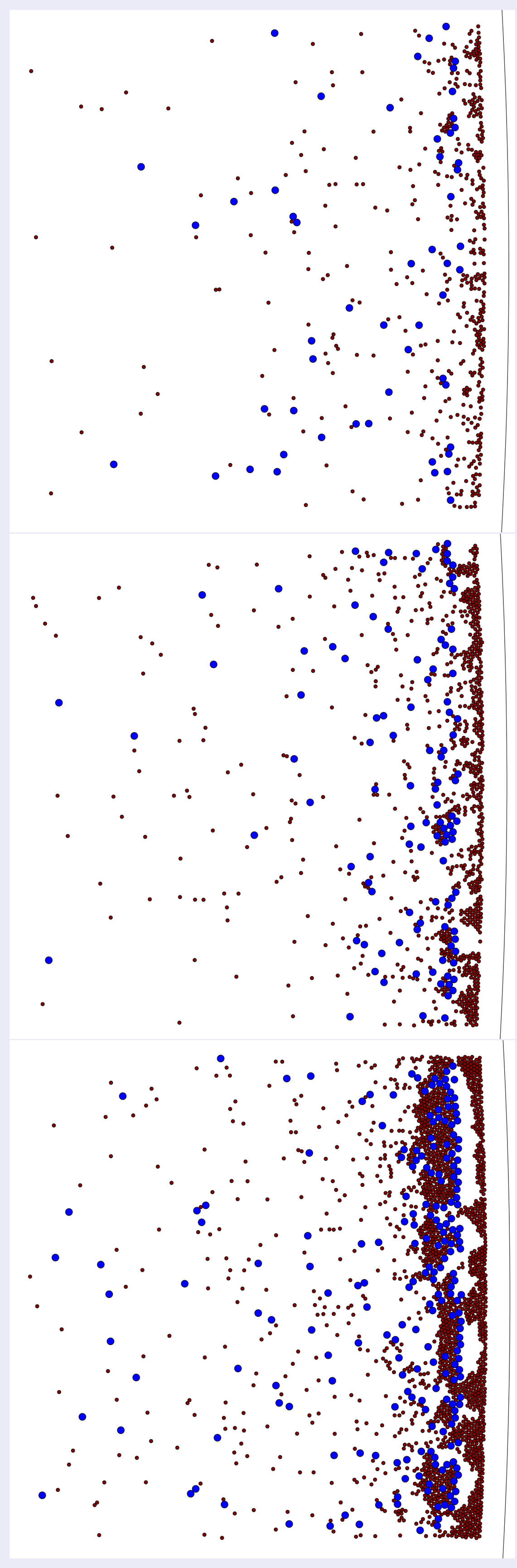

Figure 5: The final sediment of particles near the contact line after evaporation has finished. Case 1 (3730x29840) is in a top, case 2 (7460x59680) is in a middle, and case 3 (14920x119360) is in a bottom.

## Acknowledgement

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## Conclusions

The simulation results showed that the particles do not reach the contact line, but accumulate at a small distance from it. The reason for this is the surface tension acting on them in areas where the thickness of the liquid layer is comparable to the size of the particles. The same mechanism affects the separation of small and large particles. Large particles deposit at a short distance from them, along with some small particles that they prevented from moving even closer to the contact line.