The Shape Dependent Coffee-Ring Effect of Colloidal Drops on a Circular Boundary

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I. INTRODUCTION

The dynamic properties of a drop of evaporating water require a mosaic of analysis to understand them. We study the way in which fluid composed of differently shaped particles sediment as liquid dries. During the drying process, hydraulic forces attach the edges of the droplet to its substrate, and capillary flow pushes particles outwards. It is often observed that these particles deposit in a ring-like fashion, otherwise known as the Coffee-Ring effect. This problem has been studied extensively in order to understand what causes the non-equilibrium system to exhibit a behavior ubiquitous in nature, and to find ways to ameliorate or eliminate the phenomenon. These investigations have focused mainly on manipulating capillary flows. In the last decade, it has been experimentally shown that uniform drying can be obtained by manipulation of particle shape contained in the evaporating liquid.

While spherical particles can pack tightly and deposit along the original edge of the droplet, ellipsoidal particles deposit uniformly: they experience long-ranged attraction to other ellipsoidal particles which exhibits itself in the formation of loosely packed structures inside the droplet. This suggests that by using ellipsoids shaped particles instead of sphere shaped particles, one can extinguish the Coffee-Ring effect.

It has been shown that the deposition of spherical particles in an evaporating droplet can be represented as a Poisson Process while the deposition of ellipsoidal particles can be modeled using a Kardar-Parisi-Zhang (KPZ) Process. We expand this idea by simulating both ellipsoidal and spherical particles as they sediment on a circular boundary. We represent spherical suspended particles undergoing capillary flow radially outwards with a random walk which culminates and restarts each time a particle reaches a shrinking boundary. We represent ellipsoidal particles with the same model while also accounting for inter particle attraction between anisotropic particles. We provide a method for visualization of the Coffee-Ring effect, and ways to visualize the avoidance of it.

II. METHODS

Particles deposit as a liquid droplet evaporates in a way described by the Poisson process for spherical particles and the KPZ process for ellipsoidal particles. We provide a model that simulates N particles of either spherical or ellipsoidal shape as they experience capillary flow and undergo Brownian motion as they sediment on a circular boundary.

A. The Random Walk

Our model uses a two dimensional random walk to simulate N_{walks} particles within the evaporating droplet diffusing, where N_{walks} is inputted by the user. While each particle starts at the center of a circular boundary, it has N_{steps} to reach a boundary while it undergoes a random walk, where N_{steps} are inputted by the user. To represent different capillary strength we assign the percentage that each particle will step radially outwards on each step. A higher probability of a radially outward step for example, represents a stronger capillary flow force. Additionally, to represent Brownian motion, for each particle we assign an equal probability that it will move clockwise or counterclockwise in the unit of one bin on each step. The random walk of each particle ends when it hits a boundary.

B. The Iterating Circular Boundary

The key aspect of our project is the ability to model particles as they sediment on a circular boundary. We create a boundary of $360n$ bins with an initial radius of $R_{initial}$, where n and $R_{initial}$ are inputted by the user. When each particle reaches a circular boundary, depending on the particle shape, the boundary is updated and a new particle walk begins to simulate the next sedimentation process. We aim to record and plot each circular boundary after all N_{walks} particles have deposited.

C. The Poisson Process Method

The Poisson process is one of the most important models used in arrival theory. In each time interval, there is a probability of one particle being counted in each bin. The probability of observing n particles arriving in one time interval is given by

$$P(n) = \frac{(\lambda t)^n}{n!} e^{-\lambda t}$$

To simulate the Poisson Process on a circular boundary, we utilize a random walk, an inherently stochastic process. In this method, when particles undergoing a random walk reach a boundary, they bin immediately if the particle can no longer move further outward radially. We simulate these particles abilities to 'pack' at large radii by inhibiting the particles ability to 'stick' to boundary points if the particle is tangential to another. If a spherical particle is adjacent to a boundary wall, not over one, the particle will bounce off of the wall.

D. The Kardar-Parisi-Zhang Method

The Kardar-Parisi-Zhang is used to model the evolution of the static and dynamically fluctuating profile of a growing interface. This simple nonlinear equation for a local growth of the profile is given by

$$\frac{\partial h(\vec{x},t)}{\partial t} = \nu \nabla^2 h + \frac{\lambda}{2}(\nabla h)^2 + \eta(\vec{x},t)$$

where h is the height of the profile. The first term on the right-hand side describes the relaxation of the interface by a surface tension ν. The second non-linear term justifies unusual growing properties of the interface. The η term represents white gaussian noise where the average $\eta = 0$

The Kardar-Parisi-Zhang(KZP) method is based on an equation that relates stochastic growth on surfaces to diffusion and local lateral correlations. Experimentally, it has been shown that ellipsoidal particles form loosely packed structures as they diffuse due to the attraction between anisotropic particles. If a particle is not only hovering over a boundary, but also adjacent to one, it will stop it's walk. We can model these particles as 'sticky' particles.

III. RESULTS

We run our model with the same initial conditions for the Poisson process simulating spherical particles and the KZP process simulating ellipsoidal particles. We simulate 7000 particles sediment as they undergo 1000 steps each. While the particles undergo Brownian motion, they are also in a capillary flow field that is set to push particles radially outward 90% of steps. The particles deposit on a boundary that initially has a radius of 100 radial units and 360 sedimentation sites.

A. The Coffee Ring Effect Exhibited by Spherical Particles Depositing

We first visualize each spherical particle's random trajectory as it sediments on the surface while it is pushed outwards due to capillary flow and Brownian motion. We

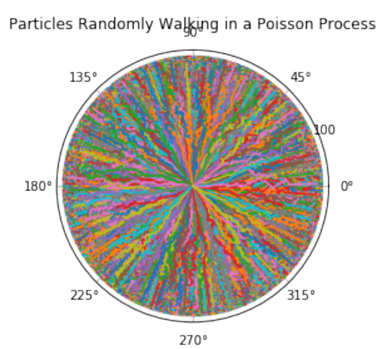

Fig. 1. Visualization of Random Walk for a Poisson Process

then plot the final boundary which contains all deposited particles.

By inspection and visual comparison to the experimental spherical coffee ring residue left by an evaporating droplet, we notice that a majority of the particles are packed

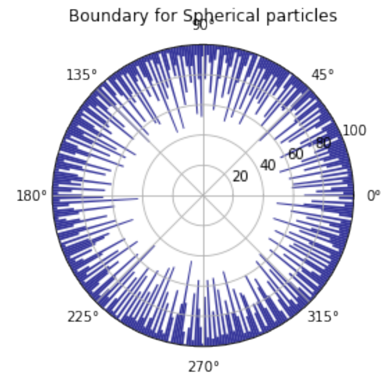

Fig. 2. Visualization of Boundary for a Poisson Process

on the boundary of the circle. We notice the rough radial boundary and can identify our Poisson model as exhibiting the Coffee-Ring effect.

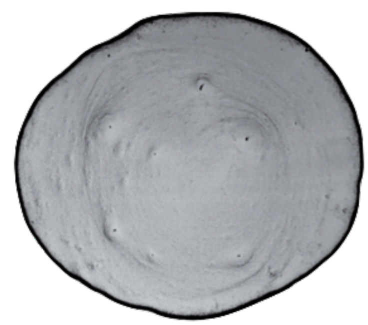

Fig. 3. Experimental Coffee Ring of Spherical Particles

B. Uniform Drying Exhibited by Ellipsoidal Particles Depositing

Next, we visualize each ellipsoidal particle's random trajectory as it sediments on the surface while it is pushed outwards due to capillary flow and Brownian motion. We

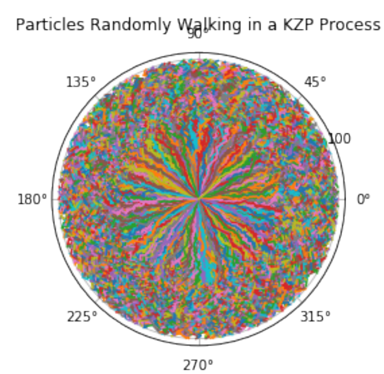

Fig. 4. Visualization of Random Walk for a KZP Process

then plot the final boundary which contains all deposited particles.

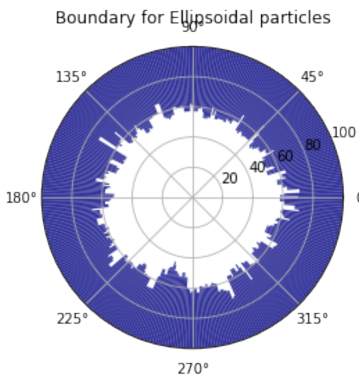

Fig. 5. Visualization of Boundary for a KZP Process

By inspection and visual comparison to the experimental ellipsoidal uniform drying stain profile left by an evaporating droplet, we notice that the majority of the particles were deposited evenly on the boundary of the circle. We can identify our KZP model as exhibiting the amelioration of the Coffee-Ring effect.

Fig. 6. Experimental Uniform Deposition of Ellipsoidal Particles

C. *Closer Analysis of Radial Stain Profile*

While our visual inspection is convincing, we wish to examine the radial stain profiles analytically. We compare the Poisson process to the KZP process on the circular boundary.

1) Effective Radius as a Function of Particle Number: In comparing the two radial profiles we expect the boundary for the KZP ellipsoidal process to shrink in radius faster than the boundary for the Poisson spherical process. We examine each model's effective radius as a function of particle number.

For each process, a line of best fit is overlain on the actual data obtained from our model of the boundary. The slope of each line represents how quickly the radius of each boundary shrinks. We observe that the rate of change of radius of the KZP process is greater than rate of change of radius of the Poisson Process as the number of particles that sediment increases. The KZP process exhibits the behavior of ellipsoidal particles while the Poisson process exhibits the behavior of spherical particles described as the Coffee-Ring

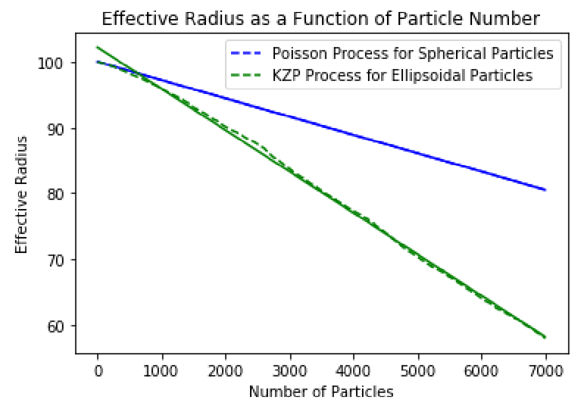

Fig. 7. Effective Radius as a Function of Particle Number

effect. We note that the radius of particles for the KZP process increases faster as particles 'stick' effectively skipping multiple sedimentation sites that the spherical model would need to fill. The growth for the Poisson process is linear, as the boundary can only increase by one particle at a time.

2) Roughness of Stain Profile as a Function Of Particle Number: We also compare the roughness of the two radial stain profiles produced by our model. Based on experimental methods, we expect the boundary created by ellipsoidal particles to have a smoother interface than the boundary created by spherical particles.

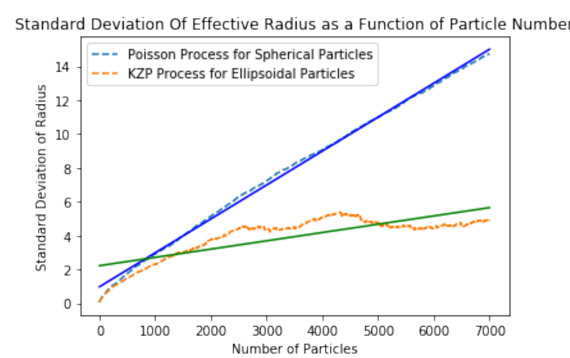

Fig. 8. Standard Deviation of as a Function of Particle Number

This graph is a way to quantify and show how rough our boundaries are. The higher the standard deviation, the rougher the surface. We see that the boundary of the Poisson Process becomes rougher as the number of particles increases. The boundary of the KZP process has a smoother interface. This is consistent with the experimental results as described by Peter Yunker.

3) Particle Density as a Function of Radius: Finally, we expect that when the Coffee-Ring effect is exhibited particle density will steadily increase as a function of radius. We examine each model's particle density as a function of particle radius.

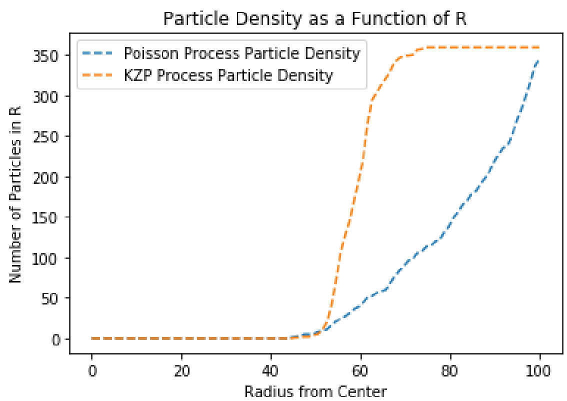

Fig. 9. Particle Density as a Function of Radius

For each process we plot the amount of particles contained as radius increases obtained from data of particles on the boundary. We see what we would expect from experimental data. The particles on the boundary of the Poisson process are primarily concentrated at the edges of the circle while the particles on the boundary of the KZP process increase as we hit an effective radius. We also are able to understand the nature of dimensionality of the boundary in noting the shape of the curves. While the ellipsoidal particles essentially create a smooth wall, the boundary of the spherical particles is rough.

IV. DISCUSSION

One of the largest drawbacks with our code is the lack of "holes" in our KZP plot. Once a particle "sticks" to another particle, we fill that bin to the current R value. A better simulation would be to suspended that single particle in the middle of bin allowing for more particles to wander into that bin and stick closer to the original boundary radius. We could not find a way to keep track and graph these holes in our model. Overall, this flaw did not seem to be a major problem as our results are consistent with real world findings.

We believe this model can be used in the future to discover what boundaries mixtures of ellipsoidal and spherical particles create. By experimenting with different amounts of each, we can find the least ellipsoidal particles needed to subdue the coffee ring effect in spherical particle mixtures. This can have useful applications in the printing, ink, and paint industries, where ring drying patterns should be avoided.

We also believe the pharmaceutical and medical industries will be interested in this research. We believe we can learn more about how colloidal drops dissolve and coat substrates. Further experimenting can be done with different drying substrates and surfaces, along with capillary forces and drying times.

V. CONCLUSIONS

We have successfully proven that our simulated model corroborates the findings in the papers published by UPENN. We effectively took a real world model and generated a more interesting computer model than the one originally published in UPENN's papers. We hope that this research can be improved upon with better code and more detailed uses of variables ,such as real world units of measurement, instead of arbitrary units of size and time. We also believe these applications are useful in many industries and should be studied further.

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