Topological and Geometrical Random Walks on Bidisperse Random Sphere Packings

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Abstract

Motivated by a problem arising from pharmaceutical science [B. Baeumer et al., Discr. Contin. Dyn. Sys. B 12], we study random walks on the contact graph of a bidisperse random sphere packing. For a random walk on the unweighted graph that terminates in a specified target set, we compare the number of steps and the euclidean distance covered. We find a linear relationship between the two metrics with a proportionality constant that can be calculated from the edge length probabilities of the contact graph.

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I. INTRODUCTION

Recently, we developed a model to predict the release kinetics of matrix tablets [1]. A matrix tablet is a device used to deliver a drug and to release it in a controlled fashion over an extended period of time. They are formulated as powder mixtures of the pharmaceutically active drug and at least two inactive ingredients, namely water soluble excipients and water insoluble polymers. Upon placement of the compressed tablet in fluid, the polymer matrix remains largely intact while soluble excipient and drug particles are dissolved and carried away by diffusion. It is of great interest to predict the time course of the drug release and its dependence on the composition of the powder mixture. In [1] we proposed a mathematical model for the drug release process, based on a discrete random walk model which serves as the starting point for the present paper.

In [1], we begin with the creation of a random dense sphere packing \( P \), see [2, 3, 7, 8] for recent discussions of this notion. Here, it will be the result of the Lubachevsky-Stillinger (LS) protocol [4, 5]. Briefly, growing spheres move and collide until the packing fraction increases only marginally between two collisions and the procedure is halted (alternatively, the pressure, the sum of the squared velocities exceeds a given threshold). From the random sphere packing so obtained, we construct the contact graph by putting an edge between sphere centers that are within a certain distance of each other. In our implementation in [1] we label some particles as “drug” particles and seek their escape routes to “exterior” particles. We count the number of steps that it takes each particle to reach one of the exterior vertices, repeating the random walk for each starting point a certain number of times. From the histograms of the number of steps we predict the cumulative release profile of the simulated matrix tablet, in good qualitative agreement with experimentally formulated matrix tablets. As we considered only monodisperse packings in [1], no distinction between topological and geometrical random walks was necessary. However, it is well possible that the powder particles of different compounds have different sizes. This leads to the question whether there is a relationship between the two metrics.
II. TOPOLOGICAL AND GEOMETRICAL RANDOM WALKS

Let $V \subset [0,1]^3$ be the set of centers of a bidisperse random sphere packing on the flat torus, where the spheres have radii $r_1 < r_2$ with $m_1$, respectively $m_2$ spheres in each class. Let vertices $x_i$ and $x_j$ be the centers of spheres with radii $r^i$ and $r^j$, respectively and fix $\varepsilon > 0$. Then $x_i$ and $x_j$ are joined by an edge in the graph $G_\varepsilon = (V,E_\varepsilon)$ if $|x_i - x_j| \leq (1+\varepsilon)(r^i + r^j)$. The infimum $\varepsilon_*$ of all $\varepsilon > 0$ such that $G_\varepsilon$ is connected, is called the level of connectedness.

Let $V_\alpha$ and $V_\omega$ be subsets of $V$, chosen randomly among all vertices $V$. We perform random walks on the graph $G_\varepsilon = (V,E_\varepsilon)$ that start in $V_\alpha$ and terminate in $V_\omega$. For simplicity, we will work with equal weights for all edges in this paper (but see the Discussion in section IV). For such a random walk we count the steps (the “topological” metric) and it’s euclidean length (i.e. the sum of the lengths of all the edges in the walk, the “geometric” metric).

Let $\pi_1$, $\pi_{12}$ and $\pi_2$ be the probabilities for an edge $e \in E_\varepsilon$ of $G_\varepsilon = (V,E_\varepsilon)$ to be (approximately) of length $2r_1$, $r_1 + r_2$ and $2r_2$, respectively. Then we expect a linear relationship

$$l(n) \asymp (2r_1\pi_1 + (r_1 + r_2)\pi_{12} + 2r_2\pi_2)n =: a_{th}n,$$

in the sense that the quotient of the two expressions approaches 1 as $n \to \infty$.

We use an implementation of the Lubachevsky-Stillinger protocol developed by the Complex Materials Theory Group at Princeton University [6] with periodic boundary conditions. Unless stated otherwise, we fix the total number of spheres to be 400. For the volume fraction $\rho$ of small sphere volume vs. the total sphere volume we have $\rho = \frac{\rho_2}{1+\xi\sigma^3}$, where $\xi = \frac{m_2}{m_1}$ and $\sigma = \frac{r_2}{r_1}$.

III. RESULTS

We consider the correlation between the packing fraction $\phi$ and the level of connectedness $\varepsilon_*$ of a packing. It is very hard to pack tightly mixtures of a small aspect ratio $\sigma^{-1} = r_1/r_2$ and a small volume fraction $\rho$ of small spheres. Geometrically, an individual small sphere may float freely in the interstitial space between the large spheres, even though the overall packing fraction may be significantly higher than the packing fraction of a monodisperse packing (see figure 1, left panel, “+”).

After creating the sphere packings, we select those that have a level of connectedness $\varepsilon_* \leq 0.05$ for the further investigations. In figure 1, right panel, we show the probabilities
FIG. 1: (Left) Plot of the level of connectedness $\varepsilon_*$ vs. the packing fraction $\phi$ of 50 respectively 100 packings for two choices of aspect ratios $\sigma^{-1}$ and volume fractions $\rho$. The termination criteria used in the Lubachevsky-Stillinger protocol are identical. An extreme case of high packing fraction but poor level of connectedness is indicated by an arrow. (Right) Probabilities for an edge to be short ($\pi_1$, solid lines) respectively long ($\pi_2$, dashed lines) as functions of the volume fraction $\rho$ of small spheres.

$\pi_1$ and $\pi_2$ of short and long edges, respectively, as functions of $\sigma^{-1}$ and $\rho$.

For each packing we create $10^4$ random walks starting at a random initial point and terminating in a random set of varying sizes. Each walk passes through a certain number of short ($2r_1$), medium ($r_1 + r_2$) and long ($2r_2$) edges. These numbers are recorded to compare them with the theoretical edge length probabilities $\pi_1$, $\pi_{12}$ and $\pi_2$ that are used in equation (1). We select all walks that share the same number of steps $n$ and take the average of their euclidean lengths, this gives the quantity $l(n)$. When we plot this against $n$, we observe a linear relationship with slope $a_{exp}$ for small values of $n$, before the points become scattered, see figure 2. The theoretical value $a_{th}$ from (1) overestimates the actual slope somewhat, but the ratio $a_{th}/a_{exp}$ between theoretical and experimental slope decreases with the size of the target set (and hence an increased average duration of the random walks), see figure 3.
FIG. 2: (Left) Plot of the average lengths of random walks of \( n \) steps on a packing of 400 spheres with \( \sigma^{-1} = 1/4 \) and a volume fraction \( \rho = 33\% \). A total of \( 10^4 \) random walks were created, ending in a target set of size 50. The solid line shows a linear fit to the data (giving the slope \( a_{exp} \)), while the dashed line has the slope predicted by equation (1), where the probabilities \( \pi_1, \pi_{12} \) and \( \pi_2 \) are taken from the contact graph. The dashed-dotted line uses the same equation, but with the empirical probabilities taken from the random walks. (Right) As in the left panel, but with \( |V_\omega| = 10 \).

IV. DISCUSSION AND CONCLUSION

The random walks considered here mimic the diffusion of a drug molecule from its original position to the edge of a matrix tablet [1]. The length distribution of these walks is used to calculate the escape times for molecules and the cumulative distribution function of the escape times is taken a prediction for the release profile of the tablet. If the particles of the powder mixture have different sizes, the definition of the “length” needs to be revisited.

Here we have provided evidence that the geometric and topological metrics on the contact graph of a random dense sphere packing are related by the formula (1), in the limit of long walks that sample correctly the edge length distribution. While the average ratio \( a_{th}/a_{exp} \) for the walks with size of the target set \( |V_\omega| = 10 \) is 1.16 (figure 3, “+”), we expect this ratio to approach 1 as the number of spheres in the packing increases. This is the focus of ongoing research.

The probabilities \( \pi_1 \) and \( \pi_2 \) are determined from contact graphs for different types of sphere mixtures. As figure 1 (right panel) suggests, these functions are monotone in both the aspect ratio \( \sigma^{-1} \) and the volume fraction \( \rho \) of the sphere mixture. We conjecture the
FIG. 3: A plot of the ratio $a_{th}/a_{exp}$ of theoretical and experimental slopes for random walks on 93 packings, with different sizes of the target sets.

The following limits

$$\lim_{\sigma^{-1} \to 0^+} \pi_1(\sigma^{-1}, \rho) = \begin{cases} 0 & \text{if } \rho = 0 \\ 1 & \text{if } \rho > 0 \end{cases}, \quad \lim_{\sigma^{-1} \to 0^+} \pi_2(\sigma^{-1}, \rho) = \begin{cases} 1 & \text{if } \rho = 0 \\ 0 & \text{if } \rho > 0 \end{cases}.$$

It is difficult to make a prediction for $\sigma^{-1} \to 1^-$, as then the distinction between short, long and medium edges disappears. Notice the change from concave to convex in $\pi_1$ as $\sigma^{-1}$ increases from 1/4 to 3/4 in the right panel of figure 1, while no change of convexity is seen in the corresponding values of $\pi_2$.

A natural generalization is to consider $k$-disperse packings with $k \geq r$ radii classes. Then there are $\frac{k(k+1)}{2}$ possible edge lengths in the contact graph and a straightforward generalization of equation (1) is expected to hold. The situation is much more complicated if the radii of the spheres themselves are a random variable.

In the present work we have considered only the case of random walks on a graph where all edges carry the same weight. The motivating problem from pharmaceutical science in [1] however required that some edges are much harder to access than others, namely those ending at particles of polymer type. Although the edge length distribution $(\pi_1, \pi_{12}, \pi_2)$ is the same, a long random walk is then no longer going to sample all edges with these probabilities. The conjectured length of random walks (1) will need to take that into account.
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