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Diffusive mixing and Tsallis entropy

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Abstract

Brownian motion, the classical diffusive process, maximizes the Boltzmann-Gibbs entropy. The Tsallis q -entropy, which is non-additive, was developed as an alternative to the classical entropy for systems in which are non-ergodic. A generalization of Brownian motion is provided that maximizes the Tsallis entropy rather than the Boltzmann-Gibbs entropy. This process is driven by a Brownian measure with a random diffusion coefficient. The distribution of this coefficient is derived as a function of q for $1 < q < 3$. Applications to transport in porous media are considered.

I. INTRODUCTION

Einstein first gave a rigorous and accurate description of diffusion in simple physical systems [1]. This description can be understood in the Eulerian framework as satisfying the diffusion equation with a constant diffusion coefficient, and in the Lagrangian framework as Brownian motion; a continuous stochastic process with stationary, independent, Gaussian increments, $X(t) - X(s), t > s > 0$, of variance $\sigma^2(t-s)$. In recent years a number of diffusive phenomena that do not fit neatly into Einstein's framework have been discovered, and these sorts of diffusion have been collectively described as being anomalous. Examples of these phenomena include diffusion in cytoplasm [2, 3] and confined nanofilms [4-6], the motion of albatrosses [7] and sharks [8], diffusion of polymers [9], and dispersion in the geophysical subsurface [10-13] among many others. One of the hallmarks of classical diffusion (*i.e.*, diffusion which is described by Brownian motion and the diffusion equation with constant diffusion coefficient) is that the mean square displacement grows linearly in time. Anomalous diffusion processes frequently do not exhibit this behavior with a power-law mean square displacement often appearing. We should point out, however, that many diffusive processes with linear mean square displacement still are anomalous [14].

A diverse set of models have been constructed to describe the behavior of anomalous diffusion phenomena. These models include continuous time random walk [15], Lévy motion [16], fractional Brownian motion [17], and many others (*e.g.*, [18]) These models frequently have power-law mean square displacements or heavy tails. In the Lagrangian framework, they can be understood to differ from Brownian motion by having interdependent, nonstationary, or non-Gaussian increments (or some combination of the three) [19]. In the Eulerian framework, they can be understood as satisfying a special case of a universal integro-differential

equation that generalizes the diffusion equation [20].

Recently, there has been an effort to understand these anomalous diffusion processes with alternative forms of entropy [21, 22]. In particular, this approach has been used to provide a statistical mechanical motivation for the frequent occurrence of Lévy distributions in physical systems [23]. When combined with generalized central limit theorems, this provides a motivation for Lévy motion in systems exhibiting anomalous diffusive behavior [23]. The argument for this is essentially as follows. If the distribution of particle displacements over a given time interval maximizes certain alternative forms of entropy, it will have a heavy tail. This places it within the domain of attraction of an α -stable Lévy distribution rather than a Gaussian distribution (in fact, a Gaussian distribution is a special case of an α -stable Lévy distribution for $\alpha = 2$). Therefore, when many independent, stationary displacements are summed the distribution will be well-approximated by an α -stable Lévy distribution. Here a particle is considered to be a traceable species in the fluid subject to diffusion.

Here we consider an alternative way to motivate anomalous diffusion using these alternative forms of entropy (Tsallis entropies [24]). This will be achieved by associating a realization of a random diffusion coefficient with each particle. The distribution of diffusion coefficients will be chosen so that the ensemble of particle displacements maximizes the Tsallis entropy. The process that results is non-ergodic and non-Markovian. The increments are not independent and they are not Gaussian. However, they are independent Gaussian if conditioned upon the diffusion coefficient.

After constructing this process, applications to flow in heterogeneous porous media will be considered. In particular, the fluctuating velocity will be informed by the random diffusion coefficient. By using an argument similar to the one presented in [23], this provides a motivation for Lévy statistics for diffusion in heterogeneous porous media. Additional

arguments can be made to provide a set of candidate velocity distributions for transport in heterogeneous porous media which are difficult to obtain in many applications.

The remainder of this manuscript is organized as follows. Section II introduces the Tsallis entropy and a closely related set of distributions called q -Gaussians. Section III describes the diffusive process with which we are concerned and derives the distribution of diffusion coefficients that maximizes the Tsallis entropy. Section IV considers applications to flow in porous media. Concluding remarks are presented in V.

II. TSALLIS ENTROPY & Q-GAUSSIANS

A generalization of the Boltzmann-Gibbs entropy has been developed by Constantino Tsallis [24] (called Tsallis entropy) and used to study a wide-range of physical processes including transport in optical lattices [25, 26], the ozone layer [27], dripping faucets [28], and astrophysics [29]. Unlike the Boltzmann-Gibbs entropy, the Tsallis entropy is non-additive. An introduction to non-extensive statistical mechanics as well as a number of applications and explorations are contained in [30].

The Boltzmann-Gibbs entropy can be derived by assuming that the four Shannon-Khinchin axioms hold [31]. These axioms state that

1. Entropy is continuous with respect to the probability distribution of states.
2. Entropy is maximal for the uniform distribution.
3. Adding a state with zero probability does not alter the entropy.
4. The entropy of a joint system $A + B$ (where $A + B$ denotes the system obtained by joining the disjoint systems A and B) is the entropy of A plus the expected value of the entropy of B conditioned on A .

The fourth axiom is the least well-motivated. If the fourth axiom is dropped, a broad family of entropies is obtained with the Tsallis entropy being a member [32]. Among these entropies, we focus on the Tsallis entropy for three reasons. One is that there are situations in which the Tsallis entropy is the simplest member of this family [33]. Another is that the q -Gaussian distributions that arise are consistent with a central-limit/renormalization group formalism [34] which has proved useful in studying many diffusive processes [13, 35, 36]. The last is that our results will be analytically tractable for the Tsallis entropy, but theoretically it is not clear how to proceed in the more general case.

A system is extensive for a given entropy, S , if $S(A+B) = S(A)+S(B)$, and non-extensive otherwise. For a set of discrete states, the Tsallis entropy is

$$S_q = \frac{1}{q-1} \left(1 - \sum_{i=1} p_i^q \right) \quad (1)$$

where p_i is the probability of being in the i^{th} state. In the limit as $q \rightarrow 1$, the Tsallis entropy reduces to the Boltzmann-Gibbs entropy. Assuming that the Tsallis entropy is the appropriate entropy for the system under examination, the value of q that produces an extensive entropy can be determined by examining the volume of phase space (the space of all possible system states) as a function of the system size [32]. For example, in a classical statistical mechanical setting the system size is determined by the number of particles and the phase space volume is given by the set of all possible position and momenta coordinates ($\Omega^N \times R^{3N}$) where Ω is the box within which the particles are contained and N is the number of particles within Ω .

For a continuous random variable X , the Tsallis entropy of X is [34]

$$S_q(X) = \frac{1}{q-1} \left(1 - \int_{-\infty}^{\infty} [f_X(x)]^q dx \right) \quad (2)$$

where $f_X(x)$ is the probability density function for X . In a dimensional system, an issue of

dimensional consistency arises – the 1 and the integral in equation 2 have different units. However, this issue is not essential, because the 1 is a carry-over from the discrete entropy so that a system without any randomness (one of the $p_i = 1$) has zero entropy. Shifting $S_q(X)$ by a constant has no impact on the maximum entropy approach that we will employ here. Random variables following a q -Gaussian distribution are maximum Tsallis entropy distributions subject to holding various statistics constant (e.g., the second moment or the second q -moment [37]). Note, however, that for fixed second moment, a q -Gaussian random variable maximizes S_{2-q} rather than S_q . The maximum entropy properties makes the q -Gaussian distribution in the context of the Tsallis entropy the analogue of the Gaussian distribution in the context of the Boltzmann-Gibbs entropy. The probability density function for a q -Gaussian is given by

$$f(x) = \frac{\sqrt{\beta}}{C_q} e_q(-\beta x^2) \quad (3)$$

where

$$e_q(x) = [1 + (1 - q)x]^{1/(1-q)} \quad (4)$$

is called the q -exponential, C_q is a normalization constant, and $\beta > 0$ is a scale parameter. In the range $1 < q < 3$, the q -Gaussian distribution is a rescaled version of the Student's t -distribution with $\nu = \frac{3-q}{q-1}$ degrees of freedom. The scaling is such that the distributions are the same if $\beta = \frac{\nu+1}{2\nu} = \frac{1}{3-q}$. We focus on this range, because we will utilize a representation of the Student's t -distribution for a key part of the analysis below.

III. RANDOM DIFFUSIVITY

Consider the stochastic differential equation

$$dX(t) = vdt + \sqrt{D}dB(t) \quad (5)$$

where $B(t)$ is a Brownian motion, and D is a random variable that is independent of $B(t)$. Here the stochastic differential equation is regarded as being conditioned on D . If the probability density function, $f_D(x)$, of D is given by

$$f_D(x) = \delta(x - D_0) \quad (6)$$

then D is a constant, and the distribution of the displacement due to diffusion, $X(t) - X(0) - vt$, is a Gaussian (note that the Gaussian distribution maximizes the Boltzmann-Gibbs entropy). This naturally leads to the question of whether or not there are distributions of D that would make the distribution of $X(t) - X(0) - vt$ maximize the Tsallis entropy. We will answer this question in the affirmative and explicitly construct the appropriate distribution for D .

Suppose that

$$D \sim D_0(\nu/V)^2 \equiv g(V) \quad (7)$$

where $V \sim \chi^2(\nu)$ is a chi-squared distribution with ν degrees of freedom and \sim denotes that two random variables have the same distribution. Then the distribution of $X(t) - X(0) - vt$ takes the form

$$X(t) - X(0) - vt \sim \sqrt{Dt}Z \quad (8)$$

$$\sim \sqrt{D_0 t} \frac{Z}{V/\nu} \quad (9)$$

where Z is a standard normal random variable. At this point, we note that a Student's t -distribution takes the form $\frac{Z}{V/\nu}$ where Z is a standard normal distribution and V is a chi-squared distribution with ν degrees of freedom [38]. Therefore, the right hand side of equation 9 is a rescaled (by a factor $\sqrt{D_0 t}$) Student's t -distribution, or, in other words, a q -Gaussian. Hence, the distribution of $X(t) - X(0) - vt$ maximizes the Tsallis entropy.

A. Probability density function for D

By changing variables in equation 7, we obtain the probability density function for D

$$\begin{aligned} f_D(x) &= f_V(g^{-1}(x)) \left| \frac{d}{dx} g^{-1}(x) \right| \\ &= \frac{1}{2^{\nu/2+1} \Gamma(\nu/2)} \exp\left(-\frac{\nu\sqrt{D_0}}{2\sqrt{x}}\right) D_0^{\nu/4} \nu^{\nu/2} x^{-\nu/4-1} \end{aligned} \quad (10)$$

This equation can be recast in terms of q by recalling that $\nu = \frac{q-3}{1-q}$. Figure 1 shows several plots of $f_D(x)$.

Note that in the limit as $q \rightarrow 1^+$ (or equivalently, $\nu \rightarrow \infty$), $f_D(x) \rightarrow \delta(x - D_0)$, so that equation 6 is satisfied in the limit. Therefore, classical advection-dispersion is recovered in the limit as $q \rightarrow 1^+$ for equation 5. This is to be expected, since $q \rightarrow 1$ corresponds to the classical Boltzmann-Gibbs entropy, and classical advection-dispersion maximizes the Boltzmann-Gibbs entropy.

IV. APPLICATION TO FLOW IN POROUS MEDIA

In subsurface hydrology, it is often assumed that the diffusion coefficient $[L^2/T]$ is

$$D = \alpha v^\beta \equiv \alpha v_e \quad (11)$$

where v is the mean velocity $[L/T]$, α is the diffusivity $[L]$, and v_e is the effective Darcy (groundwater flow) velocity $[L/T]$ [39, 40]. While this equation may be reasonable in a relatively homogeneous medium, it is likely to be problematic in highly heterogeneous formations [10–13, 41–44].

Imagine that equation 11 is applied to a medium contained in a cube. Now imagine that the cube is divided into 8 subcubes, and equation 11 is applied to each of these subcubes. If the cube is homogeneous on this scale, the mean velocity, the diffusivity, and the exponent, β ,

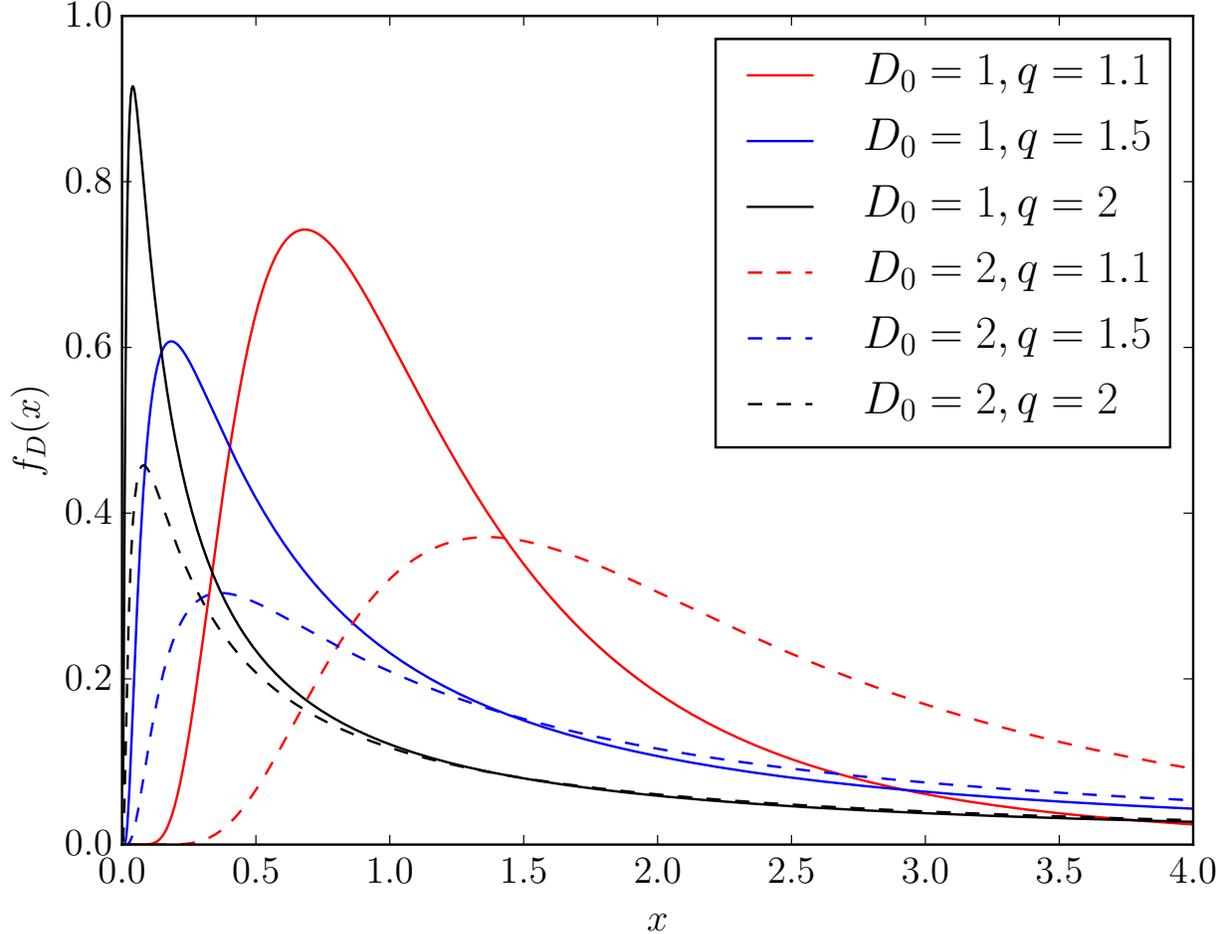


FIG. 1. (Color online) Several plots of $f_D(x)$ for several combinations of q and D_0 .

will be the same for each of the subcubes. If, on the other hand, the medium is heterogeneous, each subcube may have a unique effective velocity and diffusivity.

Suppose that we can continue dividing the subcubes until each subcube is homogeneous and that the scale of these subcubes is large enough (larger than some representative elementary volume [45]) so that equation 11 still makes sense. In this way, each subcube will have a random diffusion coefficient. The distributions in section III above provide a natural set of candidates for the distribution of the diffusion coefficient. The distribution of the random diffusion coefficient will depend on spatial temporal properties of the flow and the

medium.

The presence and importance of heterogeneity in subsurface transport is well established. We only highlight it here. The point we wish to make is that principles of maximum entropy can provide insight into the nature of the heterogeneity and its impact on advective transport.

A. Anomalous diffusion

A number of theories have been proposed to explain anomalous diffusive behavior in the subsurface [13, 14, 46–50]. We show how the maximum entropy methods employed here can be used to inform two of these models. That is, using the stochastic differential

$$dX(t) = v(X(t))dt + \sqrt{D(X(t))}dB(t) \quad (12)$$

on a mesoscale with the spatially variable diffusion coefficient having the distribution given in 10 and obeying equation 11, we can draw conclusions about the velocity field, $v(X(t))$. The first approach that we explore concerns the fractional in space advective-diffusive equation [47] and its Lagrangian underpinning, α -stable Lévy motion [16]. We show how this can arise under suitable correlations between the parameters in each of the subcubes. The second approach is based on a model where the velocity is a Markov process with velocity transitions after traveling a fixed distance [48, 49]. This approach is suitable under a different set of correlations between the parameters in each of the subcubes.

We note that this approach also reduces to classical advection-dispersion in the case of a homogeneous medium. For such a medium, the velocity and dispersion coefficients are constant. Restating this in terms of the random dispersion coefficient approach that we explore here, the velocity and dispersion coefficients follow a delta distribution. Such a

distribution is recovered in the limit as $q \rightarrow 1^+$, as discussed previously. This is what we would expect from advection-dispersion in a homogeneous medium – that the Boltzmann-Gibbs entropy applies.

1. *Connection to Lévy diffusion*

Suppose that D follows the distribution given in equation III A with $\nu \leq 2$ ($q \geq 5/3$), that $\alpha \leq \alpha_0$ and $\beta = 1$ in equation 11. Therefore,

$$\langle v^2 \rangle = \left\langle \left[\frac{D}{\alpha} \right]^2 \right\rangle \geq \left\langle \left[\frac{D}{\alpha_0} \right]^2 \right\rangle = \frac{\langle D^2 \rangle}{\alpha_0^2} \quad (13)$$

Since D has an infinite second moment, v also has an infinite second moment. Therefore, v has a heavy tail.

Suppose that the distribution of diffusion coefficients (hence velocities) is defined as follows. There are sequences of subcubes, along the flow paths within the entire domain, with equivalent flow velocities. Additionally, suppose that the number of subcubes in these sequences is proportional to the velocity. Also suppose that different subcube sequences have velocities that are independent of one another. In this way, the velocity will remain relatively constant over a time interval proportional to Nl/v , where l is the length of the subcube sides and n is the number of subcubes in the sequence along the flow path. In the case of fracture flow, the subcube sequences may represent fractures with uniform apertures (permeabilities) that are proportional to the fracture lengths (typically, fractures with smaller aperture are shorter, and fractures with larger aperture are longer [51]). Since N is proportional to v , the velocity remains relatively constant over a constant time interval, Δt . Neglecting diffusion within each subcube, the position of a particle in the flow domain can then be described as

$$X(n\Delta t) = \sum_{i=1}^n v_i \Delta t \quad (14)$$

where v_i is the velocity of the particle as it traverses the i^{th} string of subcubes. Since the distribution of v has a heavy tail, the relevant central limit distribution for $X(n\Delta t)$ is an α -stable distribution [16] rather than the normal distribution. This is consistent with the application of the fractional advection diffusion equation in subsurface hydrology [47]

2. Connection to spatially Markovian transport models

Suppose that D follows the distribution given in section III A and that α is constant. Within a subcube a particle undergoing advection and diffusion follows the stochastic differential equation

$$dX(t) = \frac{D(X(t))}{\alpha}dt + \sqrt{D(X(t))}dB(t) \quad (15)$$

where $D(X(t))$ is a spatial stochastic process that for fixed t has density given by equation 10. Using equation 11 with $\beta = 1$, this can be rewritten in terms of the mean velocity

$$dX(t) = v(X(t))dt + \sqrt{\alpha v(X(t))}dB(t) \quad (16)$$

The distribution of v can be determined with a change of variables,

$$f_v(x) = \frac{f_D(\alpha x)}{\alpha} \quad (17)$$

where we have again assumed that $\beta = 1$ in equation 11.

If diffusion is neglected, the time, dt , to traverse a subcube of length dx with mean velocity v is given by

$$dt = \frac{dx}{v(X(t))} \quad (18)$$

If diffusion is not neglected, we define dt to be the first passage time across the downstream boundary of the subcube. With this definition, dt follows the one-sided first passage time

distribution for a Brownian motion with drift. That is, dt follows an inverse Gaussian distribution with mean $dx/v(X(t))$ and shape parameter $\frac{(dx)^2}{\alpha v(X(t))}$ [52].

This answers the question of how long it will take to traverse one such subcube, but does not resolve the question of how long it will take to traverse two or more subcubes. The latter is an important question, because to understand transport across a heterogeneous field, it is necessary to understand the travel time across more than one (many) subcubes. In general, this is a difficult question, but an answer can be given by utilizing a spatially Markovian approach [48, 49]. In a spatially Markovian model, after a particle travels a fixed distance dx with a velocity $v_1 = v(X(t))$, it transitions to a new, random velocity $v_2 = v(X(t) + dx)$ whose distribution depends on v_1 , but not on prior velocities. We consider an example where the velocity transitions are determined via the Metropolis algorithm [53]. For simplicity, set $\alpha = 1 [L]$ in equation 17 and $D_0 = 1 [L^2/T]$ in equation 10. The subsequent figures will depend upon the proposal distribution used in the Metropolis algorithm. Here we have chosen the proposal distribution for x_{n+1} to be normal with mean x_n and variance 0.1. Figures 2, 4, and 6 depict histograms of particle positions obtained using this approach. Note that as q increases, the mode moves backward, but the tails of the position distribution become heavier. Figures 3, 5, and 7 show the velocity transition matrix (similar to figure 7 in [48]). To produce these figures, the velocity distribution was split into 50 bins of equal likelihood, and the color (darkness in the print version) represent the logarithm of transitioning from one bin to another after traveling length 1 $[L]$. Note that as q increases, the probability of transitioning from one velocity bin to a distant velocity bin decreases. Also, for tail velocities, the probability of transitioning to distant bins becomes very small.

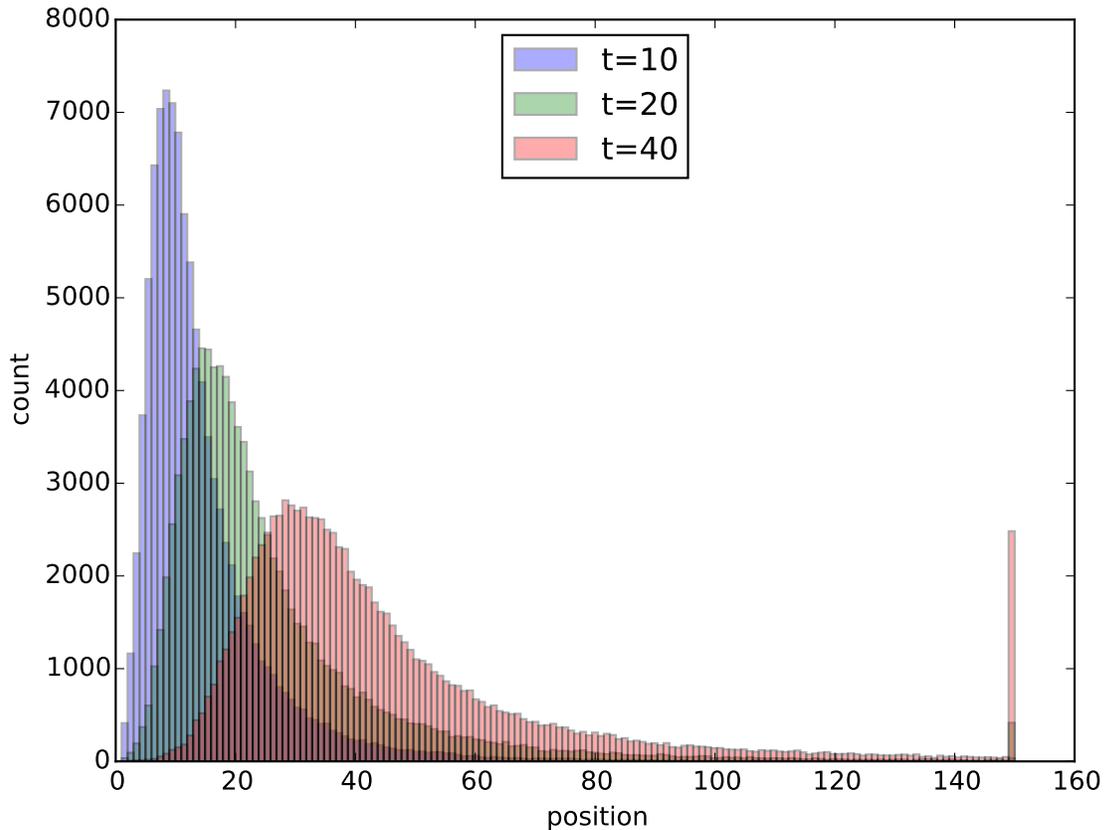


FIG. 2. (Color online) Histograms of particle positions at $t = 0, 25, 50$ for spatially Markovian model discussed in section IV A 2 with $q = 1.1$. The bar at position 150 denotes the number of particles whose position is greater than or equal to 150.

V. CONCLUSION

Diffusion in porous media frequently does not exhibit Gaussian behavior. Therefore, such diffusions do not maximize the Boltzmann-Gibbs entropy, and we hypothesize that alternative forms of entropy may be suitable. We have derived a distribution of diffusion coefficients that result in diffusion which maximizes the Tsallis entropy. This distribution was then linked to the spatio-temporal heterogeneity of the medium and the flow field. Upon making simple assumptions about the relationship between the velocity and the diffusion

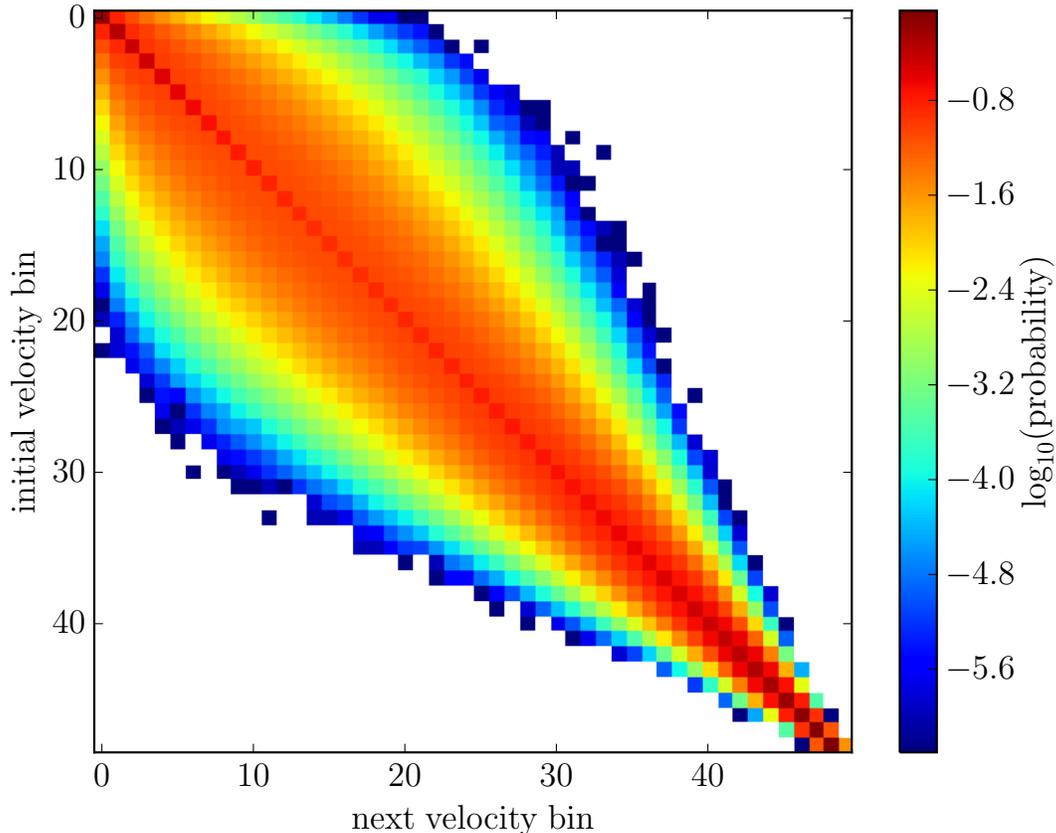


FIG. 3. (Color online) Velocity transition matrix with $q = 1.1$. The color (darkness in the print version) represents the base 10 logarithm of the probability of transitioning from a given column to a given row.

coefficient, we were able to derive estimates for the velocity distribution.

Using this velocity distribution, theoretical connections to two common models of anomalous diffusion in subsurface transport were explored. In one case, it was shown how the heavy-tails in the velocity distribution could lead to Lévy diffusion. This provides a maximum-entropy motivation for the use of these distributions in data analyses and models of subsurface contaminant transport. In the other case, connections to spatially Markov models of transport were explored. The velocity distribution needed within these models had pre-

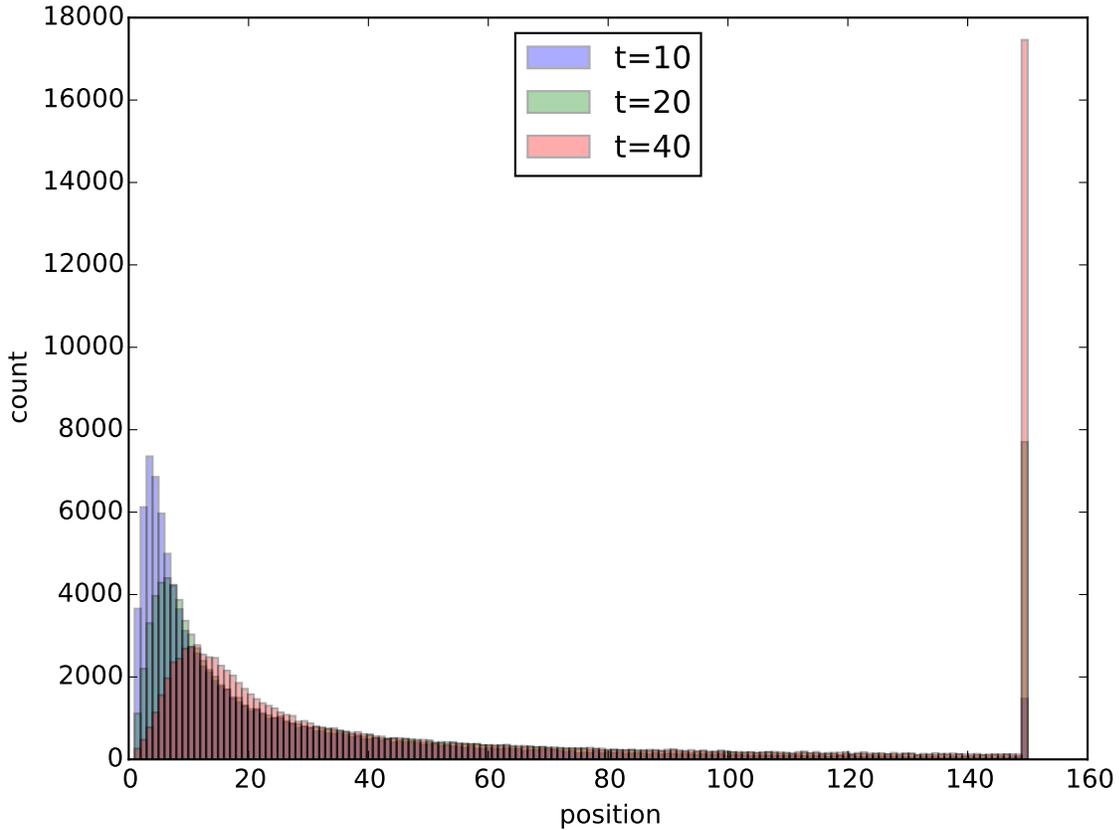


FIG. 4. (Color online) Histograms of particle positions at $t = 0, 25, 50$ for spatially Markovian model discussed in section IV A 2 with $q = 1.5$. The bar at position 150 denotes the number of particles whose position is greater than or equal to 150.

viously been obtained from numerical simulations and experiments with artificial porous media. The arguments presented here provide a set of velocity distributions derived from principles of maximum entropy that can be used to inform this type of spatially Markov model at the field scale.

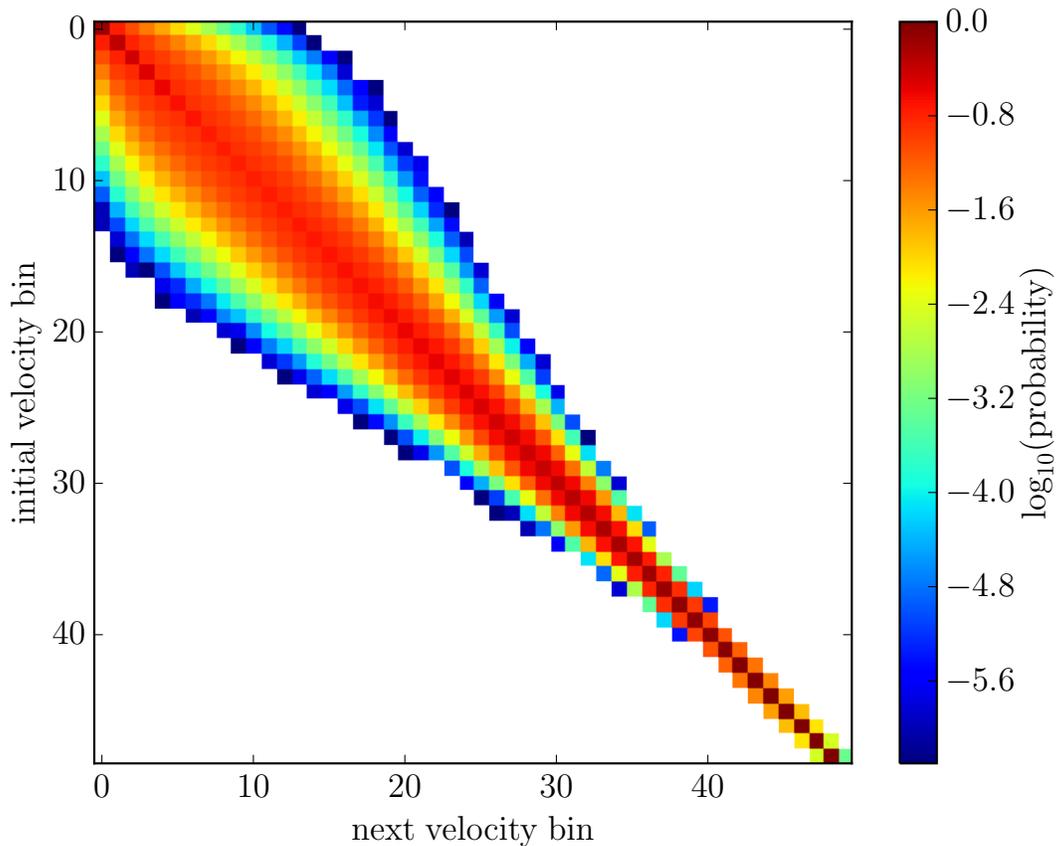


FIG. 5. (Color online) Velocity transition matrix with $q = 1.5$. The color (darkness in the print version) represents the base 10 logarithm of the probability of transitioning from a given column to a given row.

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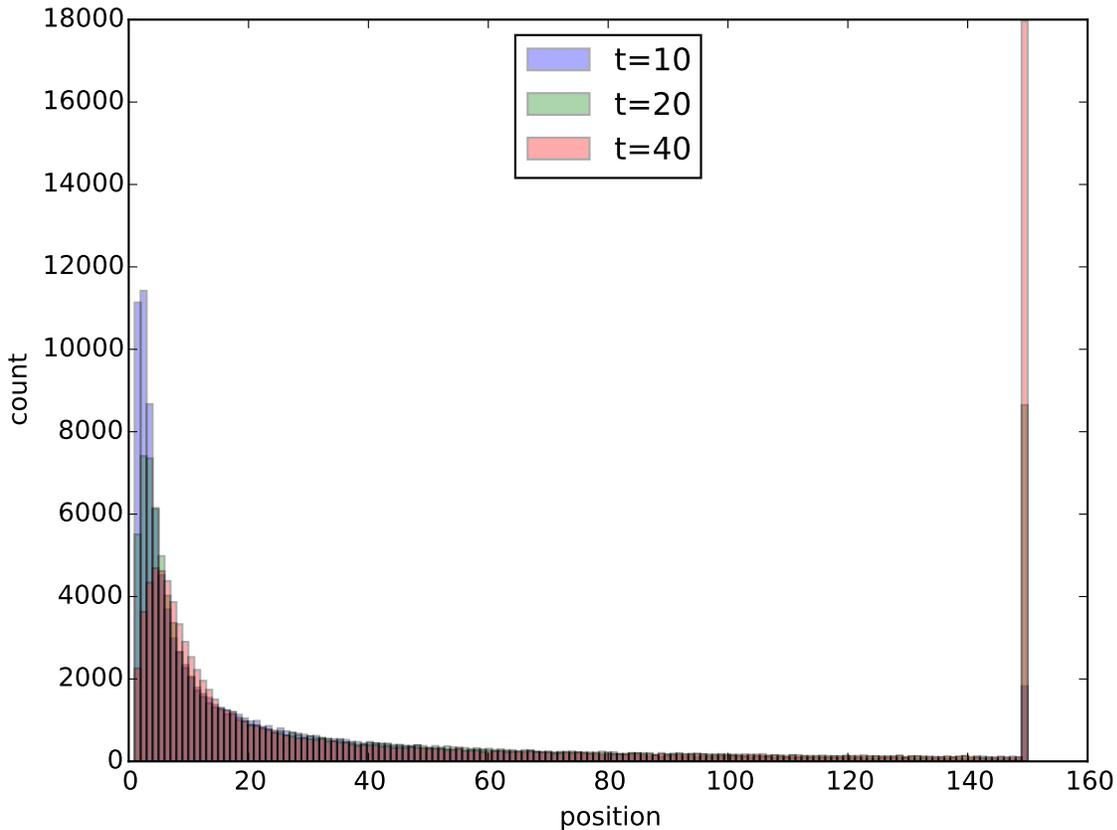


FIG. 6. (Color online) Histograms of particle positions at $t = 0, 25, 50$ for spatially Markovian model discussed in section IV A 2 with $q = 2.0$. The bar at position 150 denotes the number of particles whose position is greater than or equal to 150.

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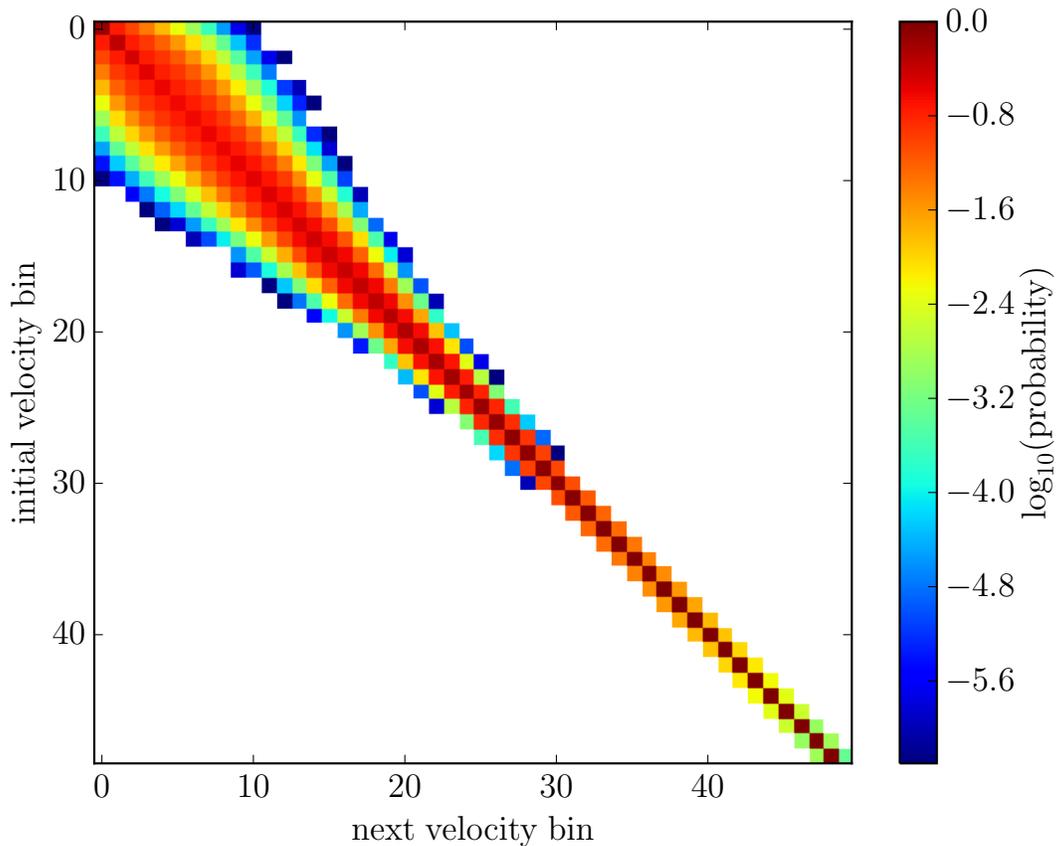


FIG. 7. (Color online) Velocity transition matrix with $q = 2.0$. The color (darkness in the print version) represents the base 10 logarithm of the probability of transitioning from a given column to a given row.

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