ANOMALOUS DIFFUSION: A DYNAMIC PERSPECTIVE

R. MURALIDHAR, D. RAMKRISHNA
School of Chemical Engineering, Purdue University, W. Lafayette, IN 47907, USA

H. NAKANISHI and D. JACOBS
Department of Physics, Purdue University, W. Lafayette, IN 47907, USA

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This paper investigates whether spontaneous, stationary velocity fluctuations can lead to deviations from the regular Fickian diffusion. A kinematic analysis reveals that anomalous diffusion, both fast and slow, arises from long-tailed velocity auto-correlation functions (VACF). This infinite span of interdependence of the random velocity leads to the breakdown of the central limit theorem for particle displacements. A generalized Langevin equation, which features a retarded friction, has been used to describe the particle dynamics in the long-time limit. The analysis reveals that simple power-law decay models for the friction kernel are adequate to yield the pathological VACFs which imply anomalous diffusion. The fluctuation dissipation theorem is invoked to infer that a fractional noise gives rise to anomalous diffusion. Such a Langevin equation represents a mean-field description of disorder effects and the friction kernel then becomes a constitutive property of the medium.

1. Introduction

Diffusion is a concept associated with random motion of particles in space. Classical or Fickian diffusion occurs when the mean squared displacement of the particle during a time interval becomes, for sufficiently long intervals, a linear function of it. In anomalous diffusion, this linearity breaks down to yield a form of diffusion either faster or slower than regular or normal (classical) diffusion. Such anomalous diffusion has unequivocally established itself to be of practical significance. Thus faster than regular diffusion has been noted in turbulence by Richardson [1] as early as 1926. More recently, diffusion in fractal media has led to several examples of slower than regular diffusion. A mathematical model describing both types of diffusion is fractional Brownian motion extensively studied by Mandelbrot and Van Ness [2].

The objective of this paper is to trace the mechanical origin of anomalous diffusion.

1 To whom correspondence should be addressed.
diffusion in a manner similar to that of regular diffusion which associates it with the classical Langevin equation. The subject of regular diffusion is most deftly dealt with in a classic paper of Chandrasekhar [3]. More specifically, the classical Langevin equation addresses the dynamics of a Brownian particle through Newton’s law by incorporating the effect of thermal fluctuations in the vicinity of the particle into a random force with suitably assigned properties. These properties are derived from the requirement that the particle velocity asymptotically attains a stationary Maxwellian distribution. Over the period of observation of the diffusing particle, the random force arising from molecular collisions undergoes such rapid fluctuations that it is approximated well by the well-known Gaussian white noise. For large time intervals \( t \), it emerges that the mean squared displacement \( \langle X(t)^2 \rangle \) becomes proportional to \( t \) with the diffusion coefficient being a sixth of the proportionality constant. Anomalous diffusion is random motion in which the foregoing proportionality of \( \langle X(t)^2 \rangle \) to \( t \) breaks down to yield the following general dependence at large \( t \):

\[
\langle X(t)^2 \rangle \sim At^{2/(2+\theta)}, \quad A > 0.
\]

For \( \theta > 0 \) we observe slow diffusion such as observed on fractals, while for \( \theta < 0 \), we obtain faster than normal diffusion. When the exponent \( \theta \) is exactly zero, normal diffusion results.

From a mathematical point of view, the phenomenon of regular diffusion is a consequence of the central limit theorem of probability (CLT) which is concerned with the statistical properties of the cumulative displacement arising from a very large number of independent displacements (which can occur in a suitably large interval). From this perspective, anomalous diffusion may be regarded as a situation where for one reason or another, the CLT becomes inapplicable.

There are several attractive attributes to the Langevin equation. First, it directly expresses Newton’s second law for a particle subject to a random force, rather than through the diffusion or Fokker–Planck equation. Indeed, the association of the Langevin equation to the diffusion equation is at the crux of the theory of Itô’s stochastic differential equation [4] which is more convenient for physical formulations than its corresponding Fokker–Plank equation. Second, because of the relationship of Brownian motion to microscopic molecular fluctuations, the Langevin equation has provided the basis of constitutive equations for nonequilibrium processes within the framework of the linear response theory (LRT) of irreversible thermodynamics. (A detailed discussion on linear response theory is presented in ref. [5].) Third, developments in Itô calculus have led to direct algorithmic solutions of stochastic differential equations which are particularly useful where their Fokker–Planck equations are difficult to solve [6].
Indeed all of the foregoing attributes of the Langevin equation make the quest for a similar approach to anomalous diffusion a reasonable one. In pursuing this problem, we first enquire into the kinematics of anomalous diffusion and seek the properties of the velocity autocorrelation function (VACF) which will lead to anomalous behavior. Based on these properties, we are able to discard the classical Langevin equation as being inconsistent with anomalous diffusion and therefore inadequate for providing it with a dynamic framework. A propitious alternative lies in the generalized Langevin equation (GLE) which views the systematic or frictional force as a linear functional of the past velocity history of the particle. The second fluctuation dissipation theorem [5] is then used to rule out the random force as being Gaussian white noise.

2. Kinematics of anomalous diffusion

In this section, we assume that the particles behave classically and execute random motion in one dimension. We relate anomalous diffusion to the normalized equilibrium velocity autocorrelation function (VACF) defined by

\[ C_V(t) = \frac{\langle V(t_0) V(t_0 + t) \rangle}{\langle V^2 \rangle}, \quad (2.1) \]

where \( V(t) \) is the velocity of the particle at time \( t \). Since the ensemble is stationary, the VACF does not depend on \( t_0 \). The VACF depicts the salient features of several stochastic trajectories in a convenient form. It offers considerable insight on the forces acting on the diffusing particle. It can be readily shown that the mean square displacement of a particle starting at the origin is given by

\[ \langle X(t)^2 \rangle = t \int_0^t C_V(\tau) \, d\tau - \int_0^t \tau C_V(\tau) \, d\tau. \quad (2.2) \]

The above equation is central to the subsequent discussion. The two terms on the right hand side may be regarded as contributions from the zeroth and first moments of the VACF over the interval \((0, t)\).

We first consider the necessary properties of the VACF to ensure anomalous diffusion.

**Proposition 1.** If \( \int_0^\infty C_V(u) \, du = D > 0 \) and \( C_V(u) = o(u^{-2}) \) as \( u \to \infty \), then \( \langle X(t)^2 \rangle = 2Dt \) as \( t \to \infty \).
The proof of this proposition is given in appendix A. The proposition says that as long as the VACF, $C_v(u)$ decays faster than $u^{-2}$ at long times, one observes normal diffusion to the leading order. A typical and well-known VACF in this category is the exponentially decaying correlation function which appears in the classical Langevin analysis of Brownian motion [3]. Another example is the VACF for Lorentz gas which has a long negative tail with a decay exponent of 2.5 in three dimensions [7]. The importance of this proposition is that it establishes that for anomalous diffusion $C_v(u)$ should decay more slowly than $u^{-2}$ for large $u$. Otherwise, it is shown in appendix A that at large times, the contribution of the second integral becomes negligible compared to that of the first ($2Dt$). This is due to a finite first moment for the VACF, i.e. $\int_0^\infty u C_v(u) \, du < \infty$. The first moment of the normalized VACF has the interpretation of the square of a characteristic time or average correlation time of the velocity fluctuations. Hence, it follows that a finite correlation time necessarily implies normal diffusion.

If the VACF decays sufficiently slowly, anomalous diffusion can result. While it is impossible to exhaust all possible functional forms for the VACF, we consider two simple models for the VACF with a view towards identifying the physics underlying anomalous diffusion.

2.1. Power-law tails

The VACF has the property that $C_v(u) \sim u^{-(1+\gamma)}$ as $u \to \infty$ with $-1 < \gamma < 1$. The nature of diffusion depends on the exponent $\gamma$. We now state the following propositions, the proofs of which are given in appendix A.

**Proposition 2a.** If $C_v(u) \sim c_0 u^{-(1-\gamma)}$ as $u \to \infty$ with $0 < \gamma < 1$, then $\langle X(t)^2 \rangle \sim Bt^{1+\gamma}$ as $t \to \infty$.

**Proposition 2b.** If $C_v(u) \sim c_0 u^{-(1+\gamma)}$ as $u \to \infty$ with $0 < \gamma < 1$ and $\int_0^\infty C_v(u) \, du = D$ with $0 < D < \infty$, then $\langle X(t)^2 \rangle \sim 2Dt$ as $t \to \infty$.

**Proposition 2c.** If $C_v(u) \sim A u^{-(1+\gamma)}$ as $u \to \infty$ with $0 < \gamma < 1$, $A < 0$ and $\int_0^\infty C_v(u) \, du = 0$, then $\langle X(t)^2 \rangle \sim Bt^{1-\gamma}$ as $t \to \infty$.

**Proposition 2d.** If $C_v(u) \sim c_0 u^{-1}$ as $u \to \infty$, then $\langle X(t)^2 \rangle \sim Bt \log t$ as $t \to \infty$.

We discuss the physical implications of the above. In case 2a, we have faster than normal diffusion because the VACF decays too slowly. Under these conditions, the contributions of the zeroth as well as the first moment of the VACF are of the same order at large times. In studies of smoke, Richardson [1]...
found that the mean squared relative displacement of two objects in a turbulent atmosphere was more rapid than that allowed by Fick's law and was given by

$$\langle X(t)^2 \rangle \sim At^3. \quad (2.3)$$

The walk exponent $\theta$ defined by eq. (1.1) for this case is $-4/3$ and eq. (2.3) is known as Richardson's two-thirds law. Analyzing this phenomenon, Shtesinger, Klafter and West [8] have argued that the successive displacements of a tracer particle in a turbulent flow field may be viewed as Lévy walks, the steps of which are positively correlated.

Proposition 2b reveals that normal diffusion can result from a slowly decaying VACF. An example of such behavior has been reported by Alder and Wainright [9] from molecular dynamics studies. In fact these investigators observed that in three dimensions the VACF decayed with a long positive tail, i.e.

$$C_v(u) \sim Au^{-1.5}, \quad u \to \infty, \quad A > 0. \quad (2.4)$$

The diffusion coefficient (the zeroth moment of the VACF) was positive. Proposition 2c pertains to slower than normal diffusion. It is well known that diffusion on fractals is anomalous [10]. The long negative tail implies anti-persistence of the fluctuating velocity. In other words, if the particle is moving in the positive $x$ direction at this instant, it is more likely to move in the negative $x$ direction in the next instant. The fluctuating velocity is thus frequently reversing its direction. The negative correlation implies a "whip-back" effect. On a fractal medium, such an effect may be interpreted as the reflections of the diffusing particle from bottlenecks and blocked ends.

Alternatively, asymptotic properties of the VACF may be derived from the asymptotic series representations for the mean squared displacement $\langle X(t)^2 \rangle$. This method has been demonstrated by Jacobs and Nakanishi [11]. Consider for instance the asymptotic representation

$$\langle X(t)^2 \rangle = \sum_{m=0}^{\infty} c_m t^{a_m}, \quad a_m < a_n \quad \text{for} \quad m > n, \quad a_0, c_0 > 0.$$ 

Under these conditions if the first and second derivatives of the mean squared displacement are monotonic for sufficiently large times, then the above series may be differentiated and we have to leading order:

$$C_v(u) \sim c_0 a_0 (a_0 - 1) t^{a_0 - 2}.$$
Since $c_0 > 0$ and $a_0 < 1$ for diffusion on fractals, we find that the VACF is negative for large times and its absolute value decays as a power law. However, differentiation of the asymptotic series for the mean squared displacement is not legitimate if the corrections to the leading behavior include oscillatory components. This has been emphasized by Jacobs and Nakanishi [11]. Analyses equivalent to propositions 2a–2d may be performed using the leading and the first correction terms in this language.

The so-called blind-ant random walks have been performed on Monte Carlo simulated percolation clusters to probe the VACF. Random walks were efficiently performed by propagating the system as a sequence of states of a Markoff chain. In order to maintain a stationary ensemble, the initial probability distribution of cluster site occupancies was chosen to be the stationary solution of the transition matrix associated with the cluster. A detailed description of the simulation procedure can be found in Jacobs and Nakanishi [11]. Fig. 1 depicts the negative tail of the VACF and the decay exponent of the absolute value. Fig. 2 shows the zeroth moment of the VACF, $\int_0^t C_v(u) \, du$, which tends to zero approximately as a power law. Table I reveals the exponents for the mean squared displacement, the zeroth moment of the VACF (denoted as $D$) and the VACF itself for the simulated blind-ant walks on various lattices. Notice that the exponent decreases by 1 at a time from $R^2$ to $D$ to VACF as predicted.

![Graph](image-url)

Fig. 1. The normalized VACF $C_v(t)$ versus discrete time (number of random steps) for the blind-ant model on a square lattice is shown. The data represent an average over 25 randomly generated percolation clusters at $p = 0.593$ with a chemical distance of 300. Because of the rapid decay, the first ten steps are shown separately on a different scale. Note that the VACF is negative for all steps except for $t = 0$ where $C_v(0) = 1$. 
Fig. 2. The integral of the normalized VACF for the blind ant of fig. 1 versus discrete time is shown. The disordered structure is responsible for the power-law decay.

Table I
Exponents for blind-ant walks.

<table>
<thead>
<tr>
<th>Model</th>
<th>( R^2 )</th>
<th>( D )</th>
<th>VACF</th>
</tr>
</thead>
<tbody>
<tr>
<td>sq bld.</td>
<td>0.71(1)</td>
<td>-0.29(2)</td>
<td>-1.27(2)</td>
</tr>
<tr>
<td>tr bld.</td>
<td>0.71(2)</td>
<td>-0.33(4)</td>
<td>-1.2(2)</td>
</tr>
<tr>
<td>sc bld.</td>
<td>0.56(2)</td>
<td>-0.48(2)</td>
<td>-1.45(5)</td>
</tr>
<tr>
<td>fcc bld.</td>
<td>0.55(2)</td>
<td>-0.43(2)</td>
<td>-1.45(5)</td>
</tr>
<tr>
<td>bcc bld.</td>
<td>0.57(2)</td>
<td>-0.46(2)</td>
<td>-1.45(5)</td>
</tr>
</tbody>
</table>

2.2. Oscillating power-law tails

The VACF in this category have as their leading behavior \( C_V(u) \sim u^{-\gamma} \cos(\omega t) \). Such oscillating VACFs have been observed by Jacobs and Nakanishi [11] in the simulation of myopic ants on bipartite lattices. The VACF of an ion in a liquid is also known to be oscillatory [12]. We now state the following proposition.

**Proposition 3.** If \( C_V(u) \sim A u^{-(1+\beta)} \cos(\omega u) - a_0 u^{-(1+\gamma)} \) as \( u \to \infty \) with \( 0 < \gamma < 1 \), \( \beta < \gamma \), \( a_0 > 0 \) and further \( \int_0^\infty C_V(u) \, du = 0 \), then \( \langle X(t)^2 \rangle \sim Bt^{(1-\gamma)} \) as \( t \to \infty \).

It is evident that if the leading behavior of the VACF is oscillatory, its integral cannot yield a monotonically increasing mean squared displacement. The proposition implies that the integral of the oscillatory component vanishes at large times and the first nonoscillating component of the VACF leads to anomalous diffusion in accordance to proposition 2c. It is worthwhile to note
that unlike in the power-law cases, the value of the leading exponent of the VACF is not smaller than that of the mean squared displacement by 2. This is because of pitfalls in differentiating asymptotic series as has been mentioned by Jacobs and Nakanishi [11]. Fig. 3 shows the highly oscillatory VACF obtained by simulating the so-called myopic-ant random walks on a bipartite percolation cluster. The VACF is even-odd, that is, it changes sign at every time step. Fig. 4 shows the time-dependent diffusion coefficient. Table II shows the relevant exponents for myopic-ant random walks.

With a view towards understanding the physics of oscillatory VACF observed on fractals, we consider the example of condensed phase kinetics such as, for example, activated barrier crossing. A solute particle at the top of the barrier may experience potential drops of order 1 eV in a few hundredths of an angstrom. The solute speed is orders of magnitude greater than the mean solvent thermal speeds and as such the solvent molecules are frozen on the time scale of solute motions. Hence, to zeroth order, the solvent exerts a conservative restoring force which reverses the solute velocity and the process starts again. To a first order, there is some cage relaxation which facilitates dissipation of the solute energy and barrier crossing. While a detailed and careful discussion of condensed phase dynamics is presented by Adelman [12], it is apparent that oscillations in the VACF of the solute occur due to the conservative cage potential, which, for small excursions of the solute motions,

Fig. 3. The normalized VACF $C_v(t)$ versus discrete time for the myopic-ant model on a square lattice is shown. The same random clusters were used as for the blind ant in fig. 1. Strong oscillations are present where the sign of the VACF is positive for all even time steps and negative for all odd time steps. Because of the fast decay, the data is presented on two vertical scales as indicated in the figure. It is clear that the even and odd time envelopes are not symmetric about zero.
is harmonic. Since the VACF for myopic-ant walks on bipartite percolation clusters is oscillatory (see fig. 3), it is possible that constraint forces that restrict the particle motions on a fractal have a conservative component.

It is evident from the above analysis that the anomalous diffusion (slow and fast) necessarily arises from long-tailed correlations. It is also apparent that the first moment of the VACF diverges signifying the absence of a characteristic time scale in the diffusion process. In physical terms, the particle velocity has effectively infinite memory of the past. The long-tailed correlations also reveal the cause for inapplicability of the CLT. Whereas in classical Langevin analysis the correlation time is finite enabling successive displacements of the particle (over time intervals much larger than the velocity auto-correlation time) to be regarded as independent, an infinite memory as in the cases considered makes this impossible. In the case of fractal diffusion, this temporal correlation appears to be a consequence of the spatial correlation of matter. An important

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**Table II**

<table>
<thead>
<tr>
<th>Model</th>
<th>$R^2$</th>
<th>$D$</th>
<th>VACF</th>
</tr>
</thead>
<tbody>
<tr>
<td>sq myp.</td>
<td>0.71(1)</td>
<td>-0.28(2)</td>
<td>e - 0.71(3)</td>
</tr>
<tr>
<td>tr myp.</td>
<td>0.71(2)</td>
<td>-0.33(4)</td>
<td>- 1.2(2)</td>
</tr>
<tr>
<td>sc myp.</td>
<td>0.57(3)</td>
<td>-0.47(3)</td>
<td>e - 0.73(2)</td>
</tr>
<tr>
<td>fcc myp.</td>
<td>0.55(4)</td>
<td>-0.43(2)</td>
<td>-1.41(8)</td>
</tr>
<tr>
<td>bcc myp.</td>
<td>0.57(2)</td>
<td>-0.46(2)</td>
<td>e - 0.61(2)</td>
</tr>
</tbody>
</table>

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Fig. 4. The integral of the normalized VACF for the myopic ant of fig. 3 versus discrete time is shown. The disordered structure is responsible for the power-law decay. Although the rapid oscillations are visible, they are much less pronounced than in the VACF. One further integration will yield the mean squared displacement which shows no visible oscillations whatsoever.
consequence of the above analysis is that it appears that the zeroth moment of the VACF vanishes for fractal diffusion. The Einstein relation or its generalized version, the first fluctuation dissipation theorem [5], yields for the complex mobility $\hat{\mu}(\omega)$,

$$\hat{\mu}(\omega) = \frac{1}{m} \int_0^\infty C_V(t) e^{i\omega t} \, dt.$$  (2.5)

The vanishing of the zeroth moment of the VACF implies that the complex mobility and, hence, the diffusion coefficient, vanishes at zero frequency [10]. Since the conductivity is proportional to the mobility, it also vanishes at zero frequency.

### 3. Generalized Langevin equation (GLE) and anomalous diffusion

In the previous section, certain forms were identified for the VACF that implied anomalous diffusion. In this section we address the question as to whether stationary velocity fluctuations can lead to anomalous diffusion. In this section we present a phenomenological GLE to describe the dynamics of the diffusing particles. We first summarize the salient aspects of the classical Langevin approach. The particle dynamics in one dimension is described by

$$\frac{dX(t)}{dt} = V(t),$$  (3.1a)

$$\frac{dV(t)}{dt} = -\gamma V(t) + \frac{F(t)}{m},$$  (3.1b)

where $m$ is the particle mass, $\gamma$ is the friction coefficient per unit mass and $F(t)$ is the random force arising from rapid thermal fluctuations. It is assumed that the random force has zero mean and is uncorrelated to particle velocity at time $t = 0$. In other words,

$$\langle F(t) \rangle = 0, \quad \langle V(0) F(t) \rangle = 0, \quad t > 0.$$  (3.2a)

In order that the Langevin equation describes stationary or equilibrium velocity fluctuations, the random force must possess the property

$$\frac{\langle F(t_0) F(t_0 + t) \rangle}{m \gamma} = k_B T \delta(t),$$  (3.2b)

where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature.
Further, in order that the velocity distribution of the particles is Maxwellian, the random force is required to be Gaussian. From the above one can deduce that the VACF becomes

\[ C_v(t) = \exp(-\gamma t) . \]  

(3.3)

Clearly, this VACF does not satisfy the necessary condition for anomalous diffusion \( C_v(u) \neq \sigma(u^{-2}) \) as \( u \to \infty \) and as such implies only normal diffusion.

The dynamics of fluctuating variables in thermal equilibrium is more generally described by the generalized Langevin equation (GLE) [5] which has a firm statistical mechanical foundation [13]. For a particle embedded in an isotropic medium, the one dimensional GLE is

\[ \frac{dV(t)}{dt} = -\int_0^t \alpha(t-\tau)V(\tau) \, d\tau + \frac{F(t)}{m}, \]  

(3.4)

where the systematic force or friction is represented by the memory integral.

The GLE reduces to the classical Langevin equation if

\[ \alpha(t) = \gamma \delta(t) . \]

In the GLE framework, one writes another GLE for \( \alpha(t) \) in terms of another memory kernel and another random noise and so on. The utility of the GLE stems from the fact that simple phenomenological models for \( \alpha(t) \) are often adequate to describe the fluctuations. The independence assumption (3.2a) and the assumption of stationarity of the fluctuating velocity leads to the second fluctuation dissipation theorem [5],

\[ \langle F(t_0) F(t_0 + t) \rangle = m^2 \langle V^2 \rangle = \alpha(t) , \]  

(3.5)

which is a generalization of the relation (3.2b). Notice that we have not invoked the equipartition theorem because it is not known if it is applicable in all situations such as, for instance, motion on a fractal medium. We enquire into the nature of the friction kernel to derive the VACF for anomalous diffusion described earlier. We consider each of the cases considered in the previous section.

We first look at certain general features of anomalous diffusion. Equation (3.4) can be rewritten as

\[ \hat{C}_v(z) = \frac{1}{z + \hat{\alpha}[z]} , \]  

(3.6)
where the hat denotes the complex Laplace transform. Observe that in the case discussed in proposition 2a, the VACF decays with an exponent less than unity and as such the zeroth moment becomes infinite. Since the zeroth moment is just the Laplace transform at zero argument, we have that

\[
\lim_{|z| \to 0} \hat{C}_V[z] = \infty \quad \text{(fast diffusion).} \tag{3.7a}
\]

This implies that the Laplace transform of the VACF is not analytic at the origin. It is immediately evident from eq. (3.6) that

\[
\lim_{|z| \to 0} \hat{\alpha}[z] = 0 \quad \text{(fast diffusion).} \tag{3.7b}
\]

In other words, the zeroth moment of the memory function (the Laplace transform at the origin) vanishes. For slow diffusion discussed in proposition 2c, we require that the zeroth moment of the VACF vanish, i.e.

\[
\lim_{|z| \to 0} \hat{C}_V[z] = 0 \quad \text{(slow diffusion).} \tag{3.8a}
\]

For this to happen, it is evident from eq. (3.6) that

\[
\lim_{|z| \to 0} \hat{\alpha}[z] = \infty \quad \text{(slow diffusion).} \tag{3.8b}
\]

Fast and slow diffusion may now be contrasted with normal diffusion. In regular diffusion, both the VACF as well as the memory function have nonvanishing and finite zeroth moments and this breaks down for anomalous diffusion. Whereas the integral of the VACF vanishes for slow diffusion, that of the memory kernel vanishes for fast diffusion.

We first consider fast diffusion and investigate if simple power-law models for the memory kernel can describe this diffusion phenomenon. More specifically, we assume the following asymptotic representation:

\[
\alpha(t) \sim \sum_{m=0}^{\infty} c_m t^{-r_m}, \quad r_m > 0, \quad m = 0, 1, 2, \ldots, \quad r_m > r_n \quad \text{for } m > n. \tag{3.9}
\]

It is shown (see appendix B) that if \( \alpha(t) \sim -d_0 t^{-(1+\gamma)} \) (0 < \( \gamma \) < 1), as \( t \to \infty \), with \( d_0 > 0 \), then the VACF decays asymptotically as \( c_0 t^{-(1-\gamma)} \), where \( c_0 \) is positive.

The nature of the dynamics can be understood in terms of the qualitative forms of the memory kernel and the VACF. The memory function is positive.
for short times, but has a negative tail so that its zeroth moment can vanish as required. From the second fluctuation dissipation theorem (3.5) it follows that

\[ \langle F(t_0) F(t_0 + t) \rangle \sim -d_0 m^2 \langle V^2 \rangle t^{-(1+\gamma)}, \quad t \rightarrow \infty, \]

(3.10)

and the spectral density of the random force \( I_F(\omega) \) has the property

\[ I_F(\omega) \sim a \omega^\gamma, \quad \omega \rightarrow 0. \]

(3.11)

The vanishing of the low-frequency components of the fluctuating force implies a very small coherence. The negative correlation of the random force at large times implies a tendency for the force to change sign at every instant. Although at first it may appear that this would retard the particle velocity significantly and, hence, slow the diffusion, it should be noted that only the nature of the total force or acceleration determines the nature of the diffusion. In this case, the irregularity of the stochastic component of this force is compensated by a negative memory kernel at large times. The positive long-tailed VACF implies coherence in the particle kinematics and, as such, faster than normal diffusion.

Next we consider slow diffusion. It is shown (see appendix B) that if

\[ a(t) \sim d_0 t^{-(1-\gamma)} \quad (0 < \gamma < 1), \]

as \( t \rightarrow \infty \) with \( d_0 > 0 \), then the VACF decays asymptotically as

\[ -c_0 t^{-(1-\gamma)}, \]

where \( c_0 \) is positive. The qualitative time dependence of the memory kernel and the VACF are opposite to those for fast diffusion. In this case, the fluctuating force auto-correlation has the asymptotic form

\[ \langle F(t_0) F(t_0 + t) \rangle \sim d_0 m^2 \langle V^2 \rangle t^{-(1-\gamma)}, \quad t \rightarrow \infty, \]

(3.12)

and its frequency spectrum has the form

\[ I_F(\omega) \sim a \omega^{\gamma}, \quad \omega \rightarrow 0, \]

(3.13)

and, as such, the low-frequency components are dominant. The random force consequently has significant correlation. Such a force would appear to push the particle along a fixed direction and thereby speed up the diffusion. However, a long-tailed positive memory kernel causes continual dissipation and the net effect is the slowing down of the diffusion. Fluctuations with a power spectrum given by eq. (3.13) are referred to as fractional noise [2].

We now discuss a case where we have a long-tailed VACF but the diffusion is regular. For a very small Brownian particle, the friction is retarded due to
hydrodynamic backflow effects and its equation of motion (one dimensional) is
\[ m^* \frac{dV}{dt} + \beta V + \alpha \int_{-\infty}^{t} (t-\tau)^{-1/2} \frac{dV}{d\tau} d\tau = F(t), \] (3.14)
where \( m^* \) is the effective mass of the particle and \( \alpha \) and \( \beta \) are constants depending on the properties of the particle and the fluid. It has been shown [5] that the VACF takes the asymptotic form
\[ C_v(\tau) \sim \frac{\sigma}{2\pi} \tau^{-3/2}, \quad \tau = \frac{\beta t}{m^*}. \] (3.15)
Notice that we have a positive and long-tailed VACF. In view of the fact that the zeroth moment is positive, we have regular diffusion although for short enough times one can have slower than normal diffusion. The presence of such a long tail was observed by Alder and Wainright [9] in the computer simulation of velocity auto-correlation functions.

4. Applications

We discuss the application of the GLE to describe diffusion on fractals. We consider specifically blind-ant random walks on percolation clusters. As expounded in section 2, the VACF in this case has a long negative tail with a vanishing zeroth moment resulting in slower than normal diffusion. One may write a phenomenological GLE to describe random motion in a fractal. In doing so, one assumes that the constraint forces restricting the particle motions to the fractal may be decomposed into systematic and stochastic components. A complete study requires a three-dimensional analysis with a tensorial friction kernel to account for spatial anisotropy in a fractal. Clearly, the friction tensor becomes an effective constitutive property of the fractal medium.

For simplicity, we have neglected anisotropic effects as a first approximation. In this case, a single parameter, the decay exponent of the friction kernel, effectively replaces the fractal medium. A simple calculation shows that the friction kernel decays as
\[ \alpha(t) \sim pt^{-2/(2+\theta)}, \quad t \to \infty, \] (4.1)
where \( \theta \) is the random-walk exponent defined in eq. (1.1).

As discussed in section 2, the VACF is long-tailed (with an infinite first moment) making it impossible to make predictions about the particle displace-
Fig. 5. Test for a Gaussian form of the probability density $P(r, t)$ in the distance traveled $r$ by the blind (square symbol) and myopic ants (diamond symbol) after time $t$ for percolation clusters at ($p = 0.593$) on the square lattice. $P(0, t)$ is the return to the origin probability density and $R(t)$ is the root mean squared displacement. The scaling assumption of $P(r, t) = P(0, t) f(r/R(t))$ is made. A Gaussian density will produce a straight line of slope = 2 for the above plot. Scaling is observed for time frames of $t = 500, 1000, 1500$ and 2000. The data presented here is an average over these four time frames with a minimum of 16 random clusters for the blind ant and 36 random clusters for the myopic ant. A total of 217 realizations were used. A straight line fit for the above data yields a slope of 1.45 indicating that the density is not a Gaussian.

ment using the central limit theorem. As such, the probability distribution of displacements cannot be Gaussian unless the fluctuating force is itself a Gaussian process. It was shown that the distribution of displacement on the fractal deviates from Gaussian [14]. Fig. 5 shows the distribution of positions obtained by us from the random walk simulation on a percolation cluster. The deviation from the Gaussian form is very transparent. It thus appears that to describe diffusion on a fractal in the GLE framework, we must choose the random force to be a non-Gaussian fractional noise.

5. Summary

The problem of anomalous diffusion has several facets and has consequently been viewed with many approaches such as continuous time random walk (CTRW) [15] and scaling models [16]. In this paper, the kinematics and dynamics of anomalous diffusion have been studied within the generalized
Langevin framework of irreversible thermodynamics. This approach has several advantages which have been discussed in section 1. A kinematic analysis shows that deviations from Fickian diffusion stem from long-tailed velocity auto-correlation having an infinite first moment. The infinite interdependence makes the applicability of the central limit theorem to the displacements of the particle invalid. In view of the fact that the VACF in anomalous diffusion does not decay exponentially, the classical Langevin equation is inappropriate and a generalized Langevin equation (GLE) is necessary. This equation features a friction term with memory (friction kernel).

It is shown that simple power-law forms for the asymptotic decay of the friction kernel give rise to the necessary long-time behavior of the VACF for both slower and faster than normal diffusion. The similarities and differences between these two types of random motion are brought out in a transparent manner. Whereas the VACFs in both cases have infinite first moments (often interpreted as absence of a characteristic time), they differ in the behavior of the zeroth moment of the VACFs and memory kernels. For fast diffusion, the friction kernel has a long negative tail and a vanishing zeroth moment. This property is possessed by the VACF for slow diffusion. The VACF for the fast diffusion has a diverging zeroth moment, a property possessed by the memory kernel for slow diffusion. The analysis reveals that spatial correlations in the fractal imply effective temporal correlations of the VACF and the random force.

Above all, the analysis establishes that stationary velocity fluctuations can lead to anomalous diffusion and no nonlinear effects are necessary. Since the GLE is not restricted to particle velocities, but in general describes the fluctuations of macrovariables of an equilibrium ensemble in the linear regime, other transport processes (such as for example the transfer of charge at a fractal interface) may be investigated. Hitherto, the GLE has been found to be convenient only when there is a time-scale separation between the primary variables and the bath variables. The analysis presented shows that one can apply it to situations with no characteristic time using simple scaling models for the friction kernel.

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Appendix A

The propositions in section 2 are simple consequences of the following theorem on asymptotic properties of integrals [17].

**Theorem 1.** Suppose that \( f(x) \) is an integrable function of the real variable \( x \) such that \( f(x) \sim x^{\nu} \) as \( x \to \infty \), where \( \nu \) is a real or complex constant. Let \( a \) be any finite real number. Then as \( x \to \infty \), we have

\[
\int_{x}^{\infty} f(t) \, dt \sim \frac{x^{\nu+1}}{\nu+1} \quad (\text{Re} \, \nu < -1),
\]

\[
\int_{a}^{x} f(t) \, dt \sim \begin{cases} 
\text{a constant} & (\text{Re} \, \nu < -1), \\
\ln x & (\nu = -1), \\
\frac{x^{\nu+1}}{\nu+1} & (\text{Re} \, \nu > -1).
\end{cases}
\]

**Proof of proposition 1.** We have

\[
\frac{\left<X(t)^2\right>}{<V^2>_t} = \int_{0}^{t} C_{\nu}(u) \, du - t^{-1} \int_{0}^{t} u C_{\nu}(u) \, du. \tag{A.1}
\]

Consider the first integral. Since \( C_{\nu}(u) = o(u^{-2}), \ V \varepsilon > 0, \ \exists \ a \ T \) such that \( |C_{\nu}(u)|/u^{-2} < \varepsilon \) for \( u \geq T \). For \( T \leq t_1 \leq t_2 \), we have

\[
\int_{t_1}^{t_2} |C_{\nu}(u)| \, du \leq \varepsilon \int_{t_1}^{t_2} u^{-2} \, du = \varepsilon \left( \frac{1}{t_1} - \frac{1}{t_2} \right) \leq \frac{\varepsilon}{t_1} \leq \frac{\varepsilon}{T}.
\]

Since \( \varepsilon \) is arbitrary,

\[
\int_{0}^{\infty} C_{\nu}(u) \, du = D < \infty.
\]

Consider the second integral in eq. (A.1). For \( t > T \), we have

\[
t^{-1} \int_{0}^{t} u C_{\nu}(u) \, du = t^{-1} \left( \int_{0}^{T} u C_{\nu}(u) \, du + \int_{T}^{t} u C_{\nu}(u) \, du \right)
\leq t^{-1} \left( \int_{0}^{T} u C_{\nu}(u) \, du + \int_{T}^{t} u |C_{\nu}(u)| \, du \right) < t^{-1} \left( \int_{0}^{T} u C_{\nu}(u) \, du + \varepsilon \int_{T}^{t} u^{-1} \, du \right).
\]
Hence, we have
\[ t^{-1} \int_0^t uC_v(u) \, du < t^{-1} \int_0^T uC_v(u) \, du + t^{-1} \epsilon (\ln t - \ln T). \]

Clearly as \( t \to \infty \), the right hand side is \( c(t^0) \) and as such does not contribute to \( \langle X(t)^2 \rangle \). Hence, we have on account of the positivity of \( D \):
\[ \langle X(t)^2 \rangle \sim 2Dt, \quad t \to \infty. \]

**Proof of proposition 2a.** On application of the theorem on asymptotic properties of integrals to the two integrals on the right-hand side of eq. (A.1) we have
\[ \frac{\langle X(t)^2 \rangle}{\langle V^2 \rangle_t} \sim \frac{At^\gamma}{\gamma} - \frac{t^{-1}At^{1+\gamma}}{1+\gamma}, \quad t \to \infty, \]
or
\[ \langle X(t)^2 \rangle \sim \frac{A\langle V^2 \rangle}{\gamma(1+\gamma)} t^{1+\gamma}, \quad t \to \infty. \]

**Proof of proposition 2b.** We have on application of theorem 1 to the integrals in eq. (A.1) for this range of \( \gamma \)
\[ \frac{\langle X(t)^2 \rangle}{\langle V^2 \rangle_t} \sim M - t^{-1}A \frac{t^{1-\gamma}}{1-\gamma}, \quad t \to \infty. \]

Hence, since \( M > 0 \),
\[ \langle X(t)^2 \rangle \sim 2Dt, \quad t \to \infty. \]

**Proof of proposition 2c.** Noting that the zeroth moment of the VACF vanishes, eq. (A.1) can be written as
\[ \frac{\langle X(t)^2 \rangle}{\langle V^2 \rangle_t} = -\int_{-\infty}^t C_v(u) \, du - t^{-1} \int_0^t uC_v(u) \, du. \quad (A.2) \]

Using the asymptotic representation of the VACF to estimate the integrals via theorem 1, we obtain
\[
\frac{\langle X(t)^2 \rangle}{\langle V^2 \rangle t} = |A| \frac{t^{-\gamma}}{\gamma} + t^{-1} |A| \frac{t^{1-\gamma}}{1-\gamma},
\]

or

\[
\langle X(t)^2 \rangle \sim \frac{|A| \langle V^2 \rangle t^{1-\gamma}}{\gamma (1-\gamma)}, \quad t \to \infty.
\]

Proof of proposition 2d. Applying theorem 1 to the two integrals on the right-hand side of eq. (A.1), we obtain that at large times

\[
\frac{\langle X(t)^2 \rangle}{\langle V^2 \rangle t} \sim A \ln t - t^{-1} At,
\]

or

\[
\langle X(t)^2 \rangle \sim At \ln t, \quad t \to \infty.
\]

Proof of proposition 3. The oscillatory part of the VACF does not contribute to the mean squared displacement as the integrals vanish by the Riemann–Lebesgue lemma. Subsequent proof is identical to that of proposition 2c.

Appendix B

The asymptotic properties of the memory function \( \alpha(t) \) are obtained using the following theorem of Handelsman and Lew [18].

Theorem 2. Let \( f(t) \) have the asymptotic expansion

\[
f(t) \sim \sum_{m=0}^{\infty} c_m t^{-r_m}, \quad t \to \infty, \quad r_m \uparrow.
\]

(The vertical arrow denotes an increasing sequence.) If no \( r_m \) is a positive integer,

\[
\hat{f}(z) \sim \sum_{m=0}^{\infty} c_m z^{m-1} \Gamma(1-r_m) + \sum_{m=0}^{\infty} z^m \frac{(-1)^m}{m!} M[f; m+1], \quad z \to 0,
\]

where \( M[f; m+1] \) is the generalized Mellin transform of \( f \) at \( m+1 \), which is the same as the \( m \)th moment of \( f \) when that moment exists, and \( \Gamma(x) \) is the gamma function.
We seek a single power-law expression for the memory function that will yield the required asymptotic decay of the VACF for anomalous diffusion. More specifically, we assume that it has the following asymptotic expansion:

$$\alpha(t) \sim \sum_{m=0}^{\infty} d_m t^{-q_m}, \quad t \to \infty, \quad q_m > 0, \quad q_m \uparrow.$$  

We assume for simplicity that no $q_m$ is a positive integer. Following theorem 2, we have

$$\hat{\alpha}[z] \sim \sum_{m=0}^{\infty} d_m z^{q_m-1} \Gamma(1-q_m) + \sum_{m=0}^{\infty} z^m (-1)^m \frac{m!}{m^m} M[\alpha; m+1], \quad z \to 0.$$  

We assume the existence of a similar asymptotic expansion for the VACF, i.e.

$$C_V(t) \sim \sum_{m=0}^{\infty} c_m t^{-r_m}, \quad t \to \infty, \quad r_m > 0, \quad r_m \uparrow.$$  

The problem is then one of relating the coefficients and exponents appearing in the asymptotic expansion of the memory function to those of the VACF from eq. (3.6) recast as

$$\hat{\alpha}[z] = \frac{1-zC_V[z]}{C_V[z]}.$$  

**Faster than normal diffusion**: For this case, we have to leading order

$$C_V(t) \sim c_0 t^{-(1-\gamma)}, \quad t \to \infty, \quad c_0 > 0, \quad 0 < \gamma < 1.$$  

Applying theorem 2, we obtain to leading order

$$\hat{C}_V[z] \sim c_0 \Gamma(\gamma) z^{-\gamma}, \quad z \to 0.$$  

Using the above in eq. (B.4) we obtain to leading order

$$\hat{\alpha}[z] \sim \frac{z^{\gamma}}{c_0 \Gamma(\gamma)} + e(z^{\gamma}), \quad z \to 0.$$  

In view of the expansion (B.2) and the fact that for this case $M[\alpha, 1] = 0$, we have that

$$\alpha(t) \sim -\frac{1}{c_0 \Gamma(\gamma) \Gamma(-\gamma)} t^{-(1+\gamma)}, \quad t \to \infty.$$
Slower than normal diffusion: The VACF has a leading behaviour given by

$$C_V(t) \sim -c_0 t^{-(1+\gamma)}, \quad t \to \infty, \quad c_0 > 0, \quad (B.7)$$

and has a vanishing zeroth moment ($M[C_V; 1]$). Hence, we have

$$\hat{C}_V[z] \sim -c_0 \Gamma(-\gamma) z^{\gamma} + o(z^{\gamma}), \quad z \to 0.$$  

From eq. (B.4) we obtain to leading order

$$\hat{\alpha}[z] \sim \frac{1}{c_0 \Gamma(-\gamma)} z^{-\gamma}, \quad z \to 0. \quad (B.8)$$

Comparing with the asymptotic representation (B.1),

$$\alpha(t) \sim \frac{1}{c_0 \Gamma(\gamma) \Gamma(-\gamma)} t^{-(1-\gamma)}, \quad t \to \infty.$$  

References