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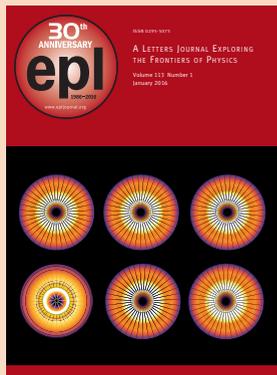
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Non-thermal Einstein relations

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Abstract – We consider a particle moving with equation of motion $\dot{x} = f(t)$, where $f(t)$ is a random function with statistics which are independent of x and t , with a finite drift velocity $v = \langle f \rangle$ and in the presence of a reflecting wall. Far away from the wall, translational invariance implies that the stationary probability distribution is $P(x) \sim \exp(\alpha x)$. A classical example of a problem of this type is sedimentation equilibrium, where α is determined by temperature. In this work we do not introduce a thermal reservoir and α is determined from the equation of motion. We consider a general approach to determining α which is not always in agreement with Einstein's relation between the mean velocity and the diffusion coefficient. We illustrate our results with a model inspired by the Boltzmann equation.

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Introduction. – This letter discusses a new perspective on a classic problem of statistical physics. Consider the motion of a particle with equation of motion

$$\frac{dx}{dt} = f(t), \quad (1)$$

where $f(t)$ is a random function, with statistical properties which are independent of x and of t . We might wish to characterise the probability distribution of the coordinate $x(t)$. We restrict ourselves to problems where space is limited by an impervious barrier, which the particle is unable to cross. We consider throughout processes with a non-zero mean drift velocity: $\langle \frac{dx}{dt} \rangle = \langle f \rangle \neq 0$, which brings the particle towards the boundary. As a result, the probability distribution has its maximum close to the wall, and decays away from it.

If we seek a probability distribution which is stationary in time, this distribution should respect, away from the boundaries, the translational invariance of the problem. Specifically, denoting $P(x)$ the stationary distribution of the particle position, the structure of P at a distance x to the wall is expected to be independent of x , provided x is large compared to the characteristic length-scale over which particles lose memory about the wall. This lengthscale is assumed to be finite, which excludes a class of systems where particles can travel arbitrarily

far from the wall over a characteristic time scale of the noise. In order to quantify the statement that the structure of the function $P(x)$ should be independent of x , we define a translation operator $\hat{T}(\Delta)$ which shifts the origin by Δ by its action on an arbitrary function $f(x)$: $\hat{T}(\Delta) f(x) = f(x - \Delta)$. The translational invariance condition can only be achieved if P is an eigenfunction of the translation operator, which satisfies $\hat{T}(\Delta)P(x) = \Lambda P(x)$ for some eigenvalue Λ . It follows that the stationary probability density must have an exponential form [1]:

$$P(x) = A \exp(\alpha x), \quad (2)$$

where A is a normalisation constant. In this letter we present a general formula determining the value of α in terms of the statistics of the function $f(t)$.

This problem is closely related to the classical treatment of sedimentation equilibrium [2] by Einstein [3] and Sutherland [4], who used statistical mechanics to describe the particle motion, in terms of a diffusion process, and to relate α to temperature via the diffusion coefficient. In this work we treat eq. (1) as a purely dynamical process, and the exponential solution (2) is a consequence of translation symmetry, rather than thermal equilibrium. We are concerned with the relation between α and dynamical quantities. In a homogeneous system, we expect the motion at long time to resemble a biased random walk with drift

velocity v and diffusion coefficient D , given by [5]

$$v = \langle f(t) \rangle, \quad D = \frac{1}{2} \int_{-\infty}^{\infty} dt \langle (f(t) - v)(f(0) - v) \rangle, \quad (3)$$

where $\langle X \rangle$ denotes the expectation value of X throughout. We assume that both v and D are finite, and non-zero. Equation (3) provides an expression for the diffusion coefficient which is valid even when the noise f has a finite correlation time [5], and not just in the case of a very short time correlation noise, relevant to a Brownian particle in a thermal bath. In the latter case, an appropriate description of the evolution of the probability distribution function (PDF), $P(x, t)$, is given by the Fokker-Planck equation:

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}(vP) + D\frac{\partial^2 P}{\partial x^2}. \quad (4)$$

Seeking a stationary solution of eq. (4) with an exponential dependence on x , eq. (2), leads to an explicit formula for α :

$$\alpha_E = \frac{v}{D}. \quad (5)$$

In the case of sedimentation equilibrium, the exponent of the exponential distribution is determined by the temperature, and eq. (5) is the basis of the relation between mobility, diffusion coefficient and temperature which was introduced by Einstein [3] and Sutherland [4]. In the remainder of this text we refer to (5) as the classical Einstein relation, although we do not consider a coupling with a thermal bath.

In general, the evolution of the probability density for the system is not always faithfully represented by (4). Although deriving the proper formulation is a challenging task (a variety of different approaches are discussed in [6–10]), our approach in this letter does *not* make explicit use of a generalisation of eq. (4), but rather uses large deviation theory [11,12]. As a consequence of the fact that eq. (4) is no more than an approximation, the status of eq. (5) is uncertain.

We analyse a simple model, where $f(t)$ is *telegraph noise*, and we determine a closed form for α , which differs from eq. (5). In the telegraph noise model, a particle moves with one of two possible velocities, and the transition between the two velocity states is completely random.

Because the exponent α is a very fundamental characterisation of the simple dynamical process (1), we provide a general analysis of this quantity. We show that large deviation theory provides a powerful approach to deriving a *generalised Einstein relation*, in the form of an implicit equation for α in terms of cumulants of $f(t)$. Equation (5) appears as an approximation of this general expression in the case where the random process f is described by a Gaussian process. The application of the general formula derived from large deviation theory is illustrated here by using the telegraph noise model as an example.

Finally, we discuss how deviations from eq. (5) could affect the sedimentation equilibrium. The telegraph noise

process can be viewed as a simplified model for the microscopic motion of molecules in gases, in which there are only two possible velocities. The analysis is readily extended to the Boltzmann equation, where atoms move ballistically between collisions, which occur at random intervals and result in an instantaneous change in the velocity of a particle. In the general case the exponent α is not given correctly by (5) for a sedimentation equilibrium described by the Boltzmann equation. This raises a question about the validity of the classical Einstein relation for sedimentation equilibrium, and potentially for other physical processes. In the limit where the suspended particles are very massive compared to the gas molecules, however, we notice that the collision term in the Boltzmann equation is replaced by a diffusion term in the particle velocity. We show that for this model equation (5) is exact, indicating that the classical Einstein relation is valid for the sedimentation equilibrium of macroscopic particles.

Telegraph noise model. – We first discuss the example where the velocity $f(t)$ in eq. (1) is a random telegraph noise. Namely, we assume that $f(t)$ can be either of the two values f_+ and f_- . The system switches from f_+ to f_- (respectively, f_- to f_+) with transition rates R_+ (respectively, R_-). The probability in the steady-state regime of the velocity to be f_+ (f_-), p_+ (respectively, p_-), is simply given by $p_+ = R_-/(R_- + R_+)$ ($p_- = R_+/(R_- + R_+)$). As a consequence, the mean velocity $\langle f \rangle$ is given by

$$\langle f \rangle = \frac{R_+f_- + R_-f_+}{R_+ + R_-}. \quad (6)$$

We assume the presence of an impervious wall, say at $x = 0$, and require that the two velocities f_+ and f_- to be of opposite signs, which allows us to impose zero flux boundary condition at the wall. In fact, in order to reach a stationary state, the zero flux condition is needed everywhere. Without any loss of generality, we assume that $f_+ > 0$, $f_- < 0$, and that the averaged velocity $\langle f \rangle$ is negative. Because the drift velocity is directed towards the wall, we expect the probability of finding a particle a distance x away from the wall decays when x increases.

We introduce the probability distribution of the position x , $P_+(x, t)$ and $P_-(x, t)$, conditioned on the value of f being equal to f_+ and f_- . Based on general arguments, presented in the introduction, we expect that the distributions P_+ and P_- decay exponentially as a function of x (see eq. (2)), and our aim here is to discuss the coefficient, α .

The evolution equation for P_+ , P_- is simply

$$\frac{\partial}{\partial t} \begin{pmatrix} P_+ \\ P_- \end{pmatrix} = -\frac{\partial}{\partial x} \begin{pmatrix} f_+ P_+ \\ f_- P_- \end{pmatrix} + \begin{pmatrix} -R_+ & R_- \\ R_+ & -R_- \end{pmatrix} \begin{pmatrix} P_+ \\ P_- \end{pmatrix}. \quad (7)$$

Steady-state solutions of the form $P_{+,-}(x) \propto A_{+,-} \exp(\alpha x)$, consistent with eq. (2), can be readily found by imposing that the matrix $M(-\alpha)$, defined by

$$M(-\alpha) \equiv \begin{pmatrix} -\alpha f_+ - R_+ & R_- \\ R_+ & -\alpha f_- - R_- \end{pmatrix} \quad (8)$$

has a zero determinant: $\det(M(\alpha)) = 0$. This condition leads to a simple algebraic equation, with only one non-zero root:

$$\alpha = -\frac{f_+ R_- + f_- R_+}{f_+ f_-}. \quad (9)$$

With our assumptions for the signs, the exponent α is negative. More generally, the product $\langle f \rangle \times \alpha > 0$. This guarantees that away from the reflecting wall, the solution decays exponentially, similar to what happens in the sedimentation problem of Brownian particles [3,4].

The value of α given by eq. (9), however, differs from the prediction given by eq. (5). From the solution of eq. (7), in the homogeneous case ($\partial/\partial x \rightarrow 0$), one determines that the correlation function decays exponentially with rate $R_- + R_+$, and by computing the variance of f we obtain the correlation function

$$\begin{aligned} & \langle (f(t) - \langle f \rangle)(f(0) - \langle f \rangle) \rangle = \\ & \frac{R_+ R_- (f_+ - f_-)^2}{(R_+ + R_-)^2} \exp[-(R_+ + R_-)t] \end{aligned} \quad (10)$$

so the diffusion coefficient D is equal to

$$D = \frac{R_+ R_-}{(R_+ + R_-)^3} (f_+ - f_-)^2. \quad (11)$$

The resulting ratio $\alpha_E = v/D$ clearly differs from the expression for α , eq. (9), thus calling for a revisiting of the Einstein-Sutherland relations. We find

$$\frac{\alpha}{\alpha_E} = -\frac{R_- R_+}{(R_- + R_+)^2} \frac{(f_+ - f_-)^2}{f_+ f_-}. \quad (12)$$

In general, this ratio may be either very large or very small. After some algebra, it can be shown that the ratio approaches unity whenever the dimensionless parameter

$$\mu = \frac{\langle f \rangle}{D} \frac{f_+ - f_-}{R_+ + R_-} \quad (13)$$

becomes very small. The quantity μ can be rewritten as $\mu = \alpha_E \ell$, where α_E is given by eq. (5), and ℓ is comparable to the mean free path of the particle. The length ℓ is the product of $1/(R_+ + R_-)$, which provides an estimate of how long the particle stays with either velocity f_+ or f_- , and of $f_+ - f_- = (f_+ - \langle f \rangle) - (f_- - \langle f \rangle)$, which is the size of the difference between the mean and the instantaneous velocity. Thus, ℓ is of the order of the size travelled by a particle between two collisions. Thus, the condition $\mu \rightarrow 0$ expresses that the mean free path, ℓ , is much smaller than the typical decay length predicted by Einstein theory.

Note that the solution $\alpha = 0$ is formally always valid. It corresponds to the homogeneous case with a uniform density of probability, which is therefore non-normalisable.

A general form for the Einstein relation. – To proceed, we now consider the general problem described by eq. (1). We consider the integral of eq. (1),

$$x(t) = x(0) + \Delta x(t), \quad \Delta x(t) = \int_0^t dt' f(t'). \quad (14)$$

The theory presented here requires the existence of all moments of Δx . Physically, this condition implies that particles move only by a finite amount over a given time interval, which excludes a class of process with algebraic tails of the distribution of f . The general conditions for the validity of our approach will be discussed later.

Let $\pi(\Delta x, t)$ be the probability density of Δx at time t . We express the condition that the distribution $P(x)$ is stationary in the form

$$P(x) = \int d\Delta x P(x - \Delta x) \pi(\Delta x, t). \quad (15)$$

Using explicitly the exponential form of the PDF $P(x)$, eq. (2), one obtains the expression

$$\int d\Delta x \exp(-\alpha \Delta x) \pi(\Delta x, t) = 1. \quad (16)$$

Equation (16) can be interpreted as the average of $\exp(-\alpha \Delta x)$, the variable $\Delta x(t)$ being characterized by its PDF, $\pi(\Delta x, t)$. It is valid provided t is much larger than the correlation time of the original process $f(t)$ so that we can assume that $\Delta x(t)$ is independent of x . This gives

$$\left\langle \exp\left(-\alpha \int_0^t dt' f(t')\right) \right\rangle = 1. \quad (17)$$

In the $t \rightarrow \infty$ limit, the large deviation principle [12] provides an appropriate approach. We introduce here the scaled cumulant generating function [12], $\lambda(k)$, defined by

$$\lambda(k) \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \ln \left\langle \exp\left(k \int_0^T dt' f(t')\right) \right\rangle \quad (18)$$

which describes the exponential growth of the average $\langle \exp(k \int_0^T dt' f(t')) \rangle$ as a function of time T . The condition expressed eq. (17) merely states that

$$\lambda(-\alpha) = 0. \quad (19)$$

Thus, the determination of spatial distribution of particles in equilibrium amounts to finding solutions of eq. (19). An elementary observation is that $\alpha = 0$ is always a root of eq. (19). The convexity of the scaled cumulant generating function [12] guarantees the existence of at most one other value of α satisfying eq. (19). The identity $\langle f \rangle = d\lambda/dk|_{k=0}$ ensures that the non-zero value of α and $\langle f \rangle$ have identical signs, as was the case for the telegraphic model.

We now illustrate the application of the large deviation theory approach by using (19) to determine α for the telegraph noise model. To this end, we discretize time, and consider $f_n = f(n\Delta t)$ and $x_n = x(n\Delta t)$, where Δt is a very small time step. Following the large deviation approach, we consider the function $\lambda(k)$, defined

by eq. (18). To evaluate $\lambda(k)$, we adapt the general approach described in [12] (see, in particular, sect. 4.3) as follows. With the telegraph noise process, f_n can take only two values, f_+ and f_- , so the integral in eq. (18) reduces (up to an overall factor Δt) to a sum of terms equal to f_+ and f_- , depending on the state of the system. The expectation value is computed by summing over all sequences $f_1, f_2, \dots, f_n, \dots$. Because the steps are statistically independent, the probability density for a sequences of steps may be expressed as a product of the form $\prod_j P(f_{j+1}, f_j)$, where $P(f_{j+1}, f_j)$ is the probability to reach f_{j+1} at $t_j + \Delta t$, if the particle is in velocity state f_j at time t_j . The summation over all possible values of f_j can be represented as a product of a string of matrices (which are 2×2 matrices, because the telegraph noise model has only two possible velocities at each time step). The quantity $\langle \exp(k\Delta t \sum_{i=0}^n f_i) \rangle$ grows exponentially as a function of n as $\xi(k)^n$, where $\xi(k)$ is the largest eigenvalue of the “tilted” transition matrix [12], given by

$$\Pi_k = \begin{pmatrix} (1 - R_+\Delta t) e^{kf_+\Delta t} & R_-\Delta t e^{kf_+\Delta t} \\ R_+\Delta t e^{kf_-\Delta t} & (1 - R_-\Delta t) e^{kf_-\Delta t} \end{pmatrix}. \quad (20)$$

Thus, $\lambda(k)$ reduces to the logarithm of the largest eigenvalue of Π_k . In the limit $\Delta t \rightarrow 0$, the matrix Π_k reduces to a sum of the identity matrix, Id, plus Δt times the matrix $M(k)$, defined by eq. (8). From this simple representation of the matrix Π_k , it immediately follows that the values of α for which $\xi(-\alpha) = 1$ in the limit $\Delta t \rightarrow 0$ are exactly the values of α for which $\det(M(-\alpha)) = 0$, thus establishing that α can be in fact established using large deviation theory. The function $\lambda(k)$ for the telegraph noise model is illustrated in fig. 1.

Equation (19) provides a simple criterion to determine α if the cumulant generating function $\lambda(k)$ can be determined. In many cases, this will not be practicable, and it is desirable to have an alternative approach. To proceed further, we notice that eq. (17) can be simply written as a series in powers of α , in the form

$$\begin{aligned} \lambda(-\alpha) &= \lim_{T \rightarrow \infty} \frac{1}{T} \ln \left\langle \sum_{n=0}^{\infty} \frac{(-\alpha)^n}{n!} \left(\int_0^T dt f(t) \right)^n \right\rangle \\ &= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} c_n \alpha^n, \end{aligned} \quad (21)$$

where c_n are defined as the integrals of the n -th order cumulants of the distribution of $f(t)$:

$$c_n = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt_1 \cdots \int_0^T dt_n \kappa[f(t_1), \dots, f(t_n)]. \quad (22)$$

The first cumulants are simply

$$\begin{aligned} \kappa[f(t_1)] &= \langle f(t_1) \rangle, \\ \kappa[f(t_1), f(t_2)] &= \langle f(t_1)f(t_2) \rangle - \langle f(t_1) \rangle^2, \\ \kappa[f(t_1), f(t_2), f(t_3)] &= \langle f(t_1)f(t_2)f(t_3) \rangle \\ &\quad - \langle f(t_1) \rangle \langle f(t_2)f(t_3) \rangle - \langle f(t_2) \rangle \langle f(t_1)f(t_3) \rangle \\ &\quad - \langle f(t_3) \rangle \langle f(t_1)f(t_2) \rangle + 2\langle f \rangle^3. \end{aligned} \quad (23)$$

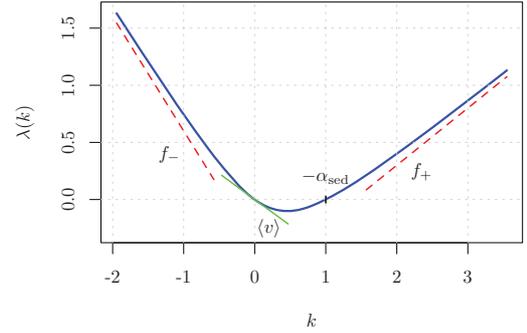


Fig. 1: (Colour online) In blue, plot of $\lambda(k)$. The parameters are $R_- = 0.4$, $R_+ = 0.7$, $f_- = -1$, and $f_+ = 0.5$, leading to $\langle f \rangle \simeq -0.45 < 0$. We remark that $\lambda'(0) = \langle f \rangle$ (green line), and that the slope of the asymptote in $k \rightarrow -\infty$ ($k \rightarrow +\infty$) is f_- (f_+) (red dotted lines). Moreover, one has $\alpha \langle f \rangle > 0$.

It is straightforward to check that the coefficients c_1 and c_2 , as defined by eq. (22) coincide with $\langle f \rangle$ and D , as defined by eq. (3). This immediately shows that the Einstein-Sutherland relations are exact when the cumulants of order higher than 3 vanish, which is the case when f is given by a Gaussian process. This conclusion does not depend on whether the process is Markovian or not.

The application of large deviation theory here rests on the existence of quantities such as the cumulant generating function introduced in eq. (18). This requires not only the existence of moments of arbitrary order of $\int^t f(t') dt'$, but also the convergence of the entire series defined with these moments, eq. (23), at least for a finite range of values of α . This makes the theory inapplicable if the probability distribution of the increments $\Delta x(t)$ defined in (14) has power-law tails.

Finally, in the telegraph model case, the parameter μ , defined in eq. (13), effectively specifies how far the process is from being Gaussian. Specifically, the deviations from a Gaussian distribution in eq. (21) are due to the terms c_n for $n > 2$. One therefore has to compare the relative importance of $c_n \alpha_E^n / n!$ for $n > 2$ with $c_1 \alpha_E$ (or, equivalently, with $c_2 \alpha_E^2 / 2$). One can show that for $n > 2$

$$\frac{c_n \alpha_E^n}{n! c_1 \alpha_E} = \mu^{n-2} G_n \left(\frac{R_-}{R_+} \right), \quad (24)$$

where the G_n are bounded functions, which implies that the solution of $\lambda(\alpha) = 0$ in the limit $\mu \rightarrow 0$ tends to $\alpha = \alpha_E$, thus justifying the Einstein equation.

More refined models of sedimentation. – Our observation that the exponent for sedimentation equilibrium in the case of a telegraph noise model does not agree with the classical Einstein relation raises the question as to whether the discrepancy exists in more refined models.

The telegraph noise model is close in structure to the Boltzmann model for the motion of atoms in a dilute gas, where the atoms move ballistically between collisions, and

have their velocities changed discontinuously at collision events which occur at random times. The difference is that the Boltzmann equation has a continuum of allowed velocities, so that the probability density is a function of a continuous velocity v and the probability density $P(x, v, t)$ satisfies a version of the Boltzmann equation in the form

$$\frac{\partial P}{\partial t}(x, v, t) = -v \frac{\partial P}{\partial x}(x, v, t) - \Gamma(v)P(x, v, t) + \int_{-\infty}^{\infty} dv' R(v, v')P(x, v', t), \quad (25)$$

where $R(v, v')$ is the rate for scattering from velocity v' to v , and $\Gamma(v) = \int_{-\infty}^{\infty} dv' R(v', v)$. Equation (25) manifestly reduces to eq. (7) when only two velocities are possible. Therefore, the analysis for eq. (25) follows the same steps as for eq. (7), except that operations involving matrix multiplication are replaced by integral transforms. The key stages in the argument are unchanged, and we conclude that in the general case the Boltzmann equation will predict that $\alpha_E \neq \alpha$.

In sedimentation problems, however, we are usually concerned with the equilibrium of colloidal particles, which are much larger than the size of the atoms. Because the mass ratio is very large, the changes in the velocity of the colloidal particle with each collision are small. This can be described by replacing the general collision term in the Boltzmann equation, eq. (25), with a diffusion term. Specifically the velocity of the particle undergoes diffusive fluctuations, with diffusion coefficient \mathcal{D} , while relaxing to a drift velocity v_0 with rate constant γ , so that v obeys the stochastic differential equation

$$dv = -\gamma(v - v_0)dt + \sqrt{2\mathcal{D}}d\eta, \quad (26)$$

where $\langle d\eta \rangle = 0$ and $\langle d\eta^2 \rangle = dt$. The corresponding Fokker-Planck equation is

$$\frac{\partial P}{\partial t} = -v \frac{\partial P}{\partial x} + \gamma \frac{\partial}{\partial v} [(v - v_0)P] + \mathcal{D} \frac{\partial^2 P}{\partial v^2}, \quad (27)$$

where the collision kernel in (25) has been replaced by a diffusion term. This is a variant of the Ornstein-Uhlenbeck process [13], which is often an accurate description of the velocity of a Brownian particle (one then speaks of a Rayleigh particle [14]). The normalisable steady-state solution of the Fokker-Planck equation, eq. (27), is

$$P(x, v) \propto \exp\left(-\frac{\gamma}{2\mathcal{D}}v^2\right) \exp\left(\frac{v_0\gamma^2}{\mathcal{D}}y\right). \quad (28)$$

Determining the spatial diffusion coefficient for the process described by (26) gives $D = \mathcal{D}/\gamma^2$, so that (28) agrees with (5). In fact, as the process described by (27) is Gaussian, the expansion in (21) reduces to its two first terms, and thus one has $\alpha = \alpha_E$. We conclude that the classical Einstein relation for sedimentation equilibrium is valid for macroscopic colloidal particles, while it may fail for

microscopic particles with a mass which is comparable to that of the gas.

Conclusions. – In this letter, we have investigated a class of stochastic problems, with a mean drift, and a reflecting wall. This corresponds to the classical and fundamental problem of sedimentation equilibrium [2–4]. Very general considerations lead to the conclusion that the distribution, far away from the wall, decays exponentially. We have shown that the decay rate, α , can be determined quite simply from large deviation theory using eq. (19) (where the cumulant generating function is available) or eq. (21) (when the cumulants of $f(t)$ are known). Whereas the classical Einstein relation can be derived from a Fokker-Planck description of the evolution of the PDF, our approach does *not* rest on any Fokker-Planck description.

In the case of the telegraph noise model we show explicitly that $\alpha \neq \alpha_E$. This raises the question as to whether there is a reason to doubt the validity of the Einstein relation for sedimentation equilibrium properties. We have argued that while α need not equal α_E for the Boltzmann equation, in the limit where the ratio of the mass of the suspended particles is very large, the Boltzmann equation should be replaced by a variant of the Ornstein-Uhlenbeck model. An explicit solution shows that $\alpha = \alpha_E$ for this case.

Lastly, it is of interest to note that in some cases the scaled cumulant generating function $\lambda(k)$ does not exist, for example when the process is discrete in time $x_{n+1} = x_n + f_n$ and the velocities are independent and follow the density of probability $p(f_n) \propto (1 + |f_n - v_0|)^{-\beta}$ with $\beta > 3$. In this case both $\langle f \rangle = v_0$ and D are finite, but $\lambda(k)$ is undefined, except at $k = 0$. The slowly decaying tails of the distribution of f_n imply that there is no region in space where the particles are not sensitive to the presence of the wall. In this case, the argument leading to the prediction of an exponential decay of the distribution P , eq. (2), is not valid.

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