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Itô–distribution from Gibbs measure and a comparison with experiment

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Langevin dynamics of a confined Brownian particle with coordinate–dependent diffusion involves multiplicative noise. Mathematically, equilibrium of such a stochastic system with multiplicative noise is an Itô–process. However, in physics literature, the process and resulting Itô–distribution is not considered to represent equilibrium because it is a modified Boltzmann distribution. Itô–distribution is derived in this paper from Gibbs measure without involving any convention for stochastic integration, hence, no Itô vs Stratonovich dilemma results. Then, in the light of an existing experiment reported in 1994 by Fauchox and Libchaber, we compare the Boltzmann distribution with the modified one for thermal equilibrium of Brownian particle near confining walls causing coordinate dependence of diffusion. Distribution corresponding to the Itô–process (modified Boltzmann) is shown to adequately account for the experimental results where the Boltzmann–distribution fails.

I. INTRODUCTION

Understanding position distribution in thermal equilibrium of a confined Brownian particle (BP) with coordinate–dependent diffusion is important for fundamental reasons and for the possibility of extensive application [1–10] across discipline. A BP near a wall or, similarly, near other BPs sees coordinate dependence of diffusion due to hydrodynamic effects [11–14]. Hydrodynamics locally renormalise diffusivity making it coordinate dependent in the proximity of walls and interfaces. This effectively lifts the symmetry (homogeneity) of space as seen by the BP even in absence of any conservative force. However, the diffusivity or damping coefficient is not known to feature in the Hamiltonian of a system in general. Coordinate dependence of diffusivity requires it to be a part of the Hamiltonian which should completely account for the inhomogeneity of space. In the present paper, the Hamiltonian of such a system is identified. The Itô–distribution is shown to result from the over-damped limit of the corresponding Gibbs measure and a comparison of the distributions is made with experimental results. The process of getting Itô–distribution in this way does not require any convention of stochastic integration and is, therefore, devoid of any Itô vs Stratonovich dilemma.

Coordinate–dependent diffusion is a stochastic problem involving multiplicative noise. Equilibrium of such a system, when considered to be an Itô–process [15], does not involve any correlated noise. However, the equilibrium that results from Itô–convention is characterized by a modified Boltzmann distribution (MBD). For example in one-dimension, the MBD is of the form

\[ P(x) = \frac{N}{D(x)} e^{-U(x)/k_B T}, \]

where \( P(x) \) is probability density at position \( x \), \( D(x) \) is coordinate–dependent diffusivity, \( U(x) \) is confining potential at minimum of which the equilibrium distribution of the particle is obtained corresponding to a constant temperature \( T \), and \( k_B \) is the Boltzmann constant. To get the MBD, local holding of the Stokes–Einstein relation \( D(x)\Gamma(x) = k_B T \) is imposed, where \( \Gamma(x) \) is coordinate–dependent damping coefficient.

On the contrary, in existing physics literature, imposition of the Boltzmann distribution (BD) has mostly been the basis of theoretically considering equilibrium in the context of coordinate–dependent diffusion [16–20]. In this connection, one treats multiplicative noise problem using the Stratonovich or a Stratonovich–like convention. The dilemma of Itô–vs–Stratonovich conventions is apparently resolved about 40 years ago by the understanding that, different conventions represent distinct physical processes [21, 22]. Therefore, in the context of thermal equilibrium, it remains to identify which convention is the correct one. Note that, the Stratonovich or Stratonovich–like conventions involve correlated (anticipating) noise. In particular, a generalization of Stratonovich convention which is known as Hänggi–Klimontovich convention also produces Boltzmann distribution for a BP with coordinate dependent diffusion. Hänggi–Klimontovich has been compared to Itô–process by Sokolov considering slow modulation of periodic potential

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diffusivity follows. The factor by which this approach is extended by making the MBD (Itô distribution) consistent with local validity of equipartition and the expression of diffusivity–dependent Hamiltonian follows. The factor $1/D(x)$ in MBD is identified to actually be a fluctuation averaged quantity $\langle 1/D(x) \rangle$ which makes every sense. The method presented here is general enough to find application in other problems where local characteristics of fluctuating diffusion is important. Diffusing diffusion is an idea of contemporary interest [29–33] particularly in the context of some non-ergodic, transient diffusion processes [34–37] and the present work could be of relevance there.

Following this, BD and MBD are compared with the results of a classic experiment reported in 1994 by Fauveux and Libchaber [38]. This experimental results has been particularly chosen for comparison of the BD to MBD because, one can do the comparison here without involving any free (adjustable) parameter. When two different functions are compared with experimental outcome, ideally, one must not use any free parameter for curve fitting and experimental results of [38] give us that opportunity. Moreover, to the knowledge of present authors, this is the only existing experimental report so far which clearly mentions failure of BD in accounting for the observations. Comparison shows MBD can capture the trend of experimental results quite well where the BD fails.

II. ITÔ–DISTRIBUTION FROM GIBBS MEASURE

Diffusivity (or diffusion constant) in uniform (for example, one-dimensional) space is defined to be $\langle (x(t) - x(0))^2 \rangle / 2t$ at time $t \to \infty$ where $x(t)$ is the position of BP at time $t$ and $\langle \ast \rangle$ stands for an ensemble average. This definition cannot hold in its entirety when the diffusivity is a local variable (function of $x$). One cannot implement the $t \to \infty$ limit keeping the particle locally confined because that will make diffusivity fall as $1/t$. The time $\tau$ over which diffusivity gets measured in one realization would depend on the length scale $\delta l$ of the locality around initial position (e.g., $x(0)$). Obviously, there would be fluctuations in $\tau$ at different realizations where $\delta l$ must be constant at all locations. Therefore, the $t \to \infty$ limit will get replaced by an ensemble average of local diffusivity on a single realization $D(x) = \delta l^2 / 2\tau$. The ensemble average would read as $\langle D(x) \rangle = \delta l^2 / \langle \tau \rangle$ where $\tau$ is, in general, bigger than the velocity–correlation time $\zeta$.

This is the crucial difference in defining local diffusivity as opposed to the uniform diffusion. Local definition according to the given form is inevitable because it must be based on the demarcation of locality on equal footing at every point in space. This definition will automatically make $D(x) \propto u(x) = \delta l / \tau$, where $u(x)$ is the average velocity of the BP on a single realization in an interval of time $\tau$ at position $x$. Existence of this length scale $\delta l$ results in the local characteristic velocity as $u(x) \sim D(x) / \delta l$. This characteristic velocity has to play its role in the local normalization of the velocity distribution which is Maxwellian everywhere in equilibrium.

A. Effective Hamiltonian and the MBD

A diffusivity–dependent effective potential is to be found out to appear in the Hamiltonian for it to take into account all the sources of inhomogeneous space. If Hamiltonian of the system does not involve in it all the inhomogeneities of space, the problem is not well-defined. It is an issue in the presence of coordinate–dependent diffusion despite diffusivity–dependent stochastic terms being added by hand to the dynamics. Hamiltonian of BP can be identified of the form

$$H = \frac{p^2}{2m} + (U(x) + F[D(x)]), \quad (1)$$
with interaction potential \( (U(x) + F[D(x)]) \) in one dimensional space. The BP of mass \( m \) has velocity \( v \) with \( p = mv \). \( F[D(x)] \) is the diffusivity dependent part of Hamiltonian which is to be found out. One can expect the structure of potential \( F[D(x)] \) is such that it should vanish for (1) uniform diffusion (diffusivity is a constant), (2) it must vanish at the over–damped limit \( m \to 0 \) because the Boltzmann factor is \( e^{-U(x)/k_B T} \) and (3) it must also vanish at \( T = 0 \) for obvious reasons. The analysis that follows in this section is, in particular, developed for the over–damped limit \( m \to 0 \) to be taken on an under–damped distribution and all the above mentioned limits will be met.

Velocity distribution being Maxwellian \( e^{-mv^2/2k_B T} \) everywhere in equilibrium, all velocities are equally likely at \( m \to 0 \) in all places. Realistically, there must be a finite upper cut–off velocity to the distribution which should be position dependent when space is inhomogeneous. This cut–off velocity should be a characteristic of the local diffusivity. Obviously, in the present case, the only candidate for cut–off is the local characteristic (average) velocity

\[
u(x) = \frac{2D(x)}{\delta l}, \tag{2}\]

which varies over realizations. Therefore, one needs to do an ensemble average over this cut-off \( u(x) \). Identifying \( \delta l \) exactly in the context of over–damped limit is not required because this constant will ultimately be absorbed in the overall normalization factor. However, the \( \delta l \) is crucial for proportionality of characteristic velocity to the diffusivity. For homogeneous diffusion, such a relation does not exist.

To have a look at the equipartition of kinetic energy with locally normalized velocity distribution, consider local normalization

\[
\int_{-u(x)}^{u(x)} dve^{-mv^2/2k_B T} = \sqrt{\frac{2k_B T}{m}} \int_{-u(x)}^{u(x)} \frac{dz}{\sqrt{2\pi}} e^{z^2} = \sqrt{\frac{2\pi k_B T}{m}} \text{erf} \left( u(x) \sqrt{\frac{m}{2k_B T}} \right) = N[u(x)], \tag{3}\]

where \( N[u(x)] = 2u(x) \) at the \( m \to 0 \). Average squared–velocity due to the Maxwellian distribution between cut–off \( \pm u(x) \) is

\[
\langle v^2 \rangle_{u(x)} = \frac{2}{N[u(x)]} \int_0^{u(x)} v^2 e^{-mv^2/2k_B T} dv = \frac{1}{N[u(x)]} \left[ \text{erf} \left( u(x) \sqrt{\frac{m}{2k_B T}} \right) - u(x) e^{-\frac{mu(x)^2}{2k_B T}} \frac{m}{2k_B T} \right].
\]

Now, expand \( N[u(x)] \) and \( e^{-\frac{mu(x)^2}{2k_B T}} \) keeping terms linear in \( m \) (under small \( m \) consideration) to get

\[
\langle v^2 \rangle_{u(x)} = \frac{1}{k_B T} \left( 1 - \frac{m u(x)^2}{6k_B T} \right) \left( 1 + \frac{m u(x)^2}{6k_B T} \right) = \frac{1}{3} u(x)^2 + O(m), \tag{4}\]

where terms independent of \( m \) will be present at the over–damped limit and all other \( O(m) \) (order \( m \)) and smaller correction terms to that expression will vanish. A small \( m \) expansion is utilized because the error function gets truncated giving closed form expressions where the ultimate goal is to take over–damped limit.

The result shown in equation (4) cannot obviously satisfy equipartition because of the coordinate dependence of \( u(x) = 2D(x)/\delta l \) which is an average velocity within a mesoscopic time interval \( \tau \). An ensemble average is due at this stage over fluctuations of \( u(x) \). Keeping in mind that \( u(x) \) has resulted from a sum over many independent velocities on even smaller time intervals within \( \tau \), the central limit theorem applies. Taking the reasonable consideration that, fluctuations result in a normal distribution \( P[u(x)] \) of \( u(x) \) at every \( x \),

\[
P[u(x)] = \frac{1}{\sqrt{2\pi \sigma}} e^{-\frac{1}{2} \left( \frac{v(x) - \langle u(x) \rangle}{\sigma} \right)^2}, \tag{5}\]

where \( \langle u(x) \rangle \) is also a function of \( x \). Doing an average (denoted by an over–line) of \( \langle v^2 \rangle_{u(x)} \) with this distribution, one finally gets

\[
\langle v^2 \rangle_{u(x)} = \langle v^2 \rangle = \frac{1}{3} u(x)^2 + O(m) = \frac{1}{3} (\langle v^2 \rangle + u(x)^2) + O(m). \tag{6}\]
The equipartition now demands \( \sigma^2 = 3k_B T/m - \langle u(x) \rangle^2 - 3\langle O(m) \rangle \) which is an expression for the width of the distribution typically at small \( m \) which is of our concern at present. At \( m \to 0 \), \( \sigma^2 \) is safely a positive number considering \( \langle u(x) \rangle \) finite. It can now be readily identified that

\[
F[D(x)] = \frac{mk_B T[D(x) - \langle D(x) \rangle]^2}{2k_B T\delta l^2 - 2m\langle D(x) \rangle^2 - \langle O(m^2) \rangle},
\]

where, at (1) \( T \to 0 \), (2) \( m \to 0 \) and (3) \( D(x) \to \) constant, \( F[D(x)] \to 0 \). Identification of \( F[D(x)] \) serves the essential purpose of including coordinate–dependent diffusivity, a source of spatial inhomogeneity, in the system’s Hamiltonian which makes the problem well defined. This well–defined system automatically justifies appearance of the complete equilibrium distribution up to a normalization factor, in general (under–damped), is

\[
P(x,v) \sim e^{-U(x)/k_B T} \left( \int_{-\infty}^{\infty} d[u(x)]P[u(x)] \frac{1}{N[u(x)]} \right) e^{-mv^2/2k_B T}
\]

\[
\sim e^{-U(x)/k_B T} \left( \frac{1}{N[u(x)]} \right) e^{-mv^2/2k_B T}.
\]

Taking the limit \( m \to 0 \) leads to \( e^{-mv^2/2k_B T} \to 1 \) and \( N[u(x)] = 2u(x) = 4D(x)/\delta l \), one gets the distribution at over–damped limit as

\[
P(x) = N \left( \frac{1}{D(x)} \right) e^{-U(x)/k_B T},
\]

where \( N \) is normalization constant over all space. This can easily be identified with the Itô–distribution by acknowledging the fact that, the 1/\( D(x) \) factor that the Itô–distribution involves is an ensemble average over local fluctuations of \( D(x) \). Thus, the Itô–distribution is arrived at as an over–damped limit of a complete under–damped distribution. In the process, one legitimately picks up an obvious physics that 1/\( D(x) \) factor being a fluctuating local quantity cannot be independent of time unless it is ensemble averaged.

Knowing the Hamiltonian, general dynamics which would be consistent with the above mentioned Itô–distribution at the over–damped limit, can now be written as

\[
m \frac{dv}{dt} = -\langle m\zeta(x) \rangle v - \frac{\partial}{\partial x} (U(x) + F[D(x)]) + \langle m\zeta(x) \rangle \sqrt{\frac{2k_B T}{\langle m\zeta(x) \rangle}} \eta(t),
\]

where \( \eta(t) \) is Gaussian white noise of unit strength and \( m\zeta(x) = \Gamma(x) \). The overdamped limit has to be understood as \( m \to 0 \) and \( \zeta(x) \to \infty \) such that \( \Gamma(x) \) is finite. At overdamped limit (\( F[D(x)] \to 0 \)), the dynamics is of the form

\[
\frac{dx}{dt} = -\frac{1}{\langle \Gamma(x) \rangle} \frac{\partial U(x)}{\partial x} + \sqrt{\frac{2k_B T}{\langle \Gamma(x) \rangle}} \eta(t),
\]

which, by the stochastic analysis using Itô–convention or equivalent Stratonovich–convention, will result in the distribution (9). The Stokes-Einstein relation \( \Gamma(x)D(x) = k_B T \) holds on each realization and reads as \( \langle \Gamma(x) \rangle = k_B T \langle \frac{1}{D(x)} \rangle \) on ensemble average. \( \langle \Gamma(x) \rangle \) is the quantity theoretically computed and, in general, is denoted by \( \Gamma(x) \) without using explicit notation for local ensemble average. It must be understood that, \( \Gamma(x) \) being a local thermodynamic quantity is independent of time on an ensemble average. In the following, we will be using the notation \( \Gamma(x) \) for \( \langle \Gamma(x) \rangle \) and \( D(x)^{-1} \) for \( \langle \frac{1}{D(x)} \rangle \) to simplify notations in keeping with standard practice.
III. COMPARISON WITH EXPERIMENT

A. The experiment

In the experiment [38], Faucheux and Libchaber observed Brownian motion of silica and latex beads (considered spheres) of diameter 1 to 3 µm in ultra–pure water confined within two clean horizontal glass plates of spacing between 6 to 1000 µm. Real–time position of the diffusing spheres on a horizontal plane (x and y coordinate) were taken by a CCD camera coupled to a microscope. A time series of about 3 minute was constructed for each of these beads, where the typical diffusion coefficient is about 1 µm²/s. Typically, 12 such time series for each bead have been taken for an ensemble average which corresponds to about half an hour of recording for each bead. The time over which the water gets contaminated in this experiment was assessed to be about a day.

Based on these time series of the horizontal positions of individual beads, diffusivity $D_{||}$ of the particles were determined over a horizontal plane which, actually, is a projection of the 3–dimensional trajectory of the bead on a plane perpendicular to the vertical. Diffusivity on the horizontal plane $D_{||}$ and that in the vertical (z) direction $D_\perp$ are functions of the distance of bead from confining horizontal glass plates. Therefore, the horizontal diffusivity of a bead measured in this projection is an average over the vertical direction (z–coordinate), where the probability density for position distribution could be the BD or MBD. Care was taken in these experiments to avoid beads coming too close to each other and interact hydro–dynamically, such that, the diffusion remains only a function of the vertical z–coordinate. For other details of the experimental determination of the $D_{||}$, one may consult [38].

B. Experimental results

Among these beads, heavier ones will have a smaller average distance from the lower glass plate, where the lighter ones will have an average height relatively larger. The diffusive excursion of these beads will be around these average height in such a way that, the average height remains stationary under steady–state (thermal equilibrium) conditions. Keeping this in mind, to plot the experimentally obtained $D_{||}$, Faucheux and Libchaber used a parameter defined as $\gamma = (h - r)/r$ where $r$ is the radius of bead and the average vertical height $h$ is defined as

$$h = \int_r^{t-r} zP_B(z)dz = \frac{e^{-r/L}(rL + L^2) - e^{(r-t)/L}([t-r]L + L^2)}{L(e^{-r/L} - e^{(r-t)/L})}, \quad (12)$$

where

$$P_B(z) = \left(\frac{1}{L}\right)\frac{e^{-z/L}}{e^{-r/L} - e^{(r-t)/L}}, \quad (13)$$

with $L = k_B T/g \Delta m$ and $\Delta m = \frac{4}{3}\pi r^3(\rho - \rho_0)$. 

![FIG. 1: Experimentally determined ratio $D_{||}/D_0$ as a function of $\gamma$](image)
In the above expressions, \( \rho \) is the density of material of the bead, \( \rho_0 \) is density of water considered in the present paper to be 1000 kg/m\(^3\) at room temperature \( T = 300 \) K, \( g \) is the acceleration due to gravity taken to be 9.8 m/s\(^2\), \( t \) is the spacing between confining plates and \( z \) (measured from the lower boundary) is the vertical coordinate of the centre of mass of the bead taken to be a sphere.

Experimentally measured \( D_\parallel \) normalized by the bulk diffusivity \( D_0 \) is plotted against the parameter \( \gamma \) (following [38]) in Fig.1. In this figure, the data-points are plotted by the symbol of square boxes and the error-bars are extracted from the Fig.4 of [38] using WebPlotDigitizer (https://apps.automeris.io/wpd/). In what follows, the same box symbol and error-bars would be used in all the figures to correspond to the experimental data-points. Relevant data is shown in the Table 1.

### C. Effect of walls on damping and diffusivity

The effect of a wall on the damping coefficients (as considered by Faucheux and Libchaber [11–14]) are well known with good support from molecular–dynamics [39]. Theoretical expression of damping coefficients are

\[
\eta_x = \eta_y \simeq \eta_0 [1 - \frac{9}{16}(r/z) + \frac{1}{8}(r/z)^3 - \frac{45}{256}(r/z)^4 - \frac{1}{16}(r/z)^5]^{-1},
\]

and

\[
\eta_z = \frac{4}{3} \eta_0 \sinh \alpha \sum_{n=1}^{\infty} \frac{n(n+1)}{(2n-1)(2n+3)} \left[ \frac{2 \sinh (2n+1)\alpha + (2n+1) \sinh 2\alpha}{4 \sinh^2(n+1/2)\alpha - (2n+1)^2 \sinh^2\alpha} - 1 \right],
\]

where \( \alpha = \cosh^{-1}(z/r) \) and \( \eta_0 \) is the damping coefficient in the bulk of the fluid which we will consider in this paper to have a value \( \eta_0 = 8.50 \times 10^{-4} \) Pa.s. The relation (15) is exact and (14) is accurate up to the order \( (r/z)^5 \). In this paper, we present results of computations up to \( n = 5 \) while using (15) to keep parity in the order of accuracy with (14), however, we have checked that going to a few orders higher in \( n \) does not appreciably change results.

Theoretical diffusivity on the horizontal plane is a constant at a particular height \( z \). Thus, we can considered those to be \( D_x = k_B T/6\pi \eta_x r \) and \( D_y = k_B T/6\pi \eta_y r \) by the same way as uniform diffusion. Average inverse of diffusivity in the vertical direction is \( D_z = 6\pi \eta_z r/k_B T \), where \( D_h(z) = D_x = D_y \) at a fixed \( z \). In this particular experiment, the vertical separation \( t \) between the confining horizontal glass plates vary from 6 to 1000 \( \mu m \). It requires to take into account presence of both the plates and the vertical distance of the bead from them when the separation \( t \) is small. Taking into account effects of both the plates at bottom and top (upper plate), Faucheux and Libchaber introduced an effective \( \eta_{x,y,z} \) as

\[
\eta_{x,y,z} = \eta_{x,y,z}^b + \eta_{x,y,z}^u - \eta_0,
\]

where the superscripts \( b \) and \( u \) indicate damping coefficients due to bottom and upper (top) plate respectively. Note that, \( \eta_{x,y,z}^b \) is a function of \( z/r \) where \( \eta_{x,y,z}^u \) is similarly a function of \( (t-z)/r \). This expression of damping coefficient \( \eta_{x,y,z} \) has nice limits. When the upper plate goes to infinity \( (t \to \infty) \), we get \( \eta_{x,y,z}^u = \eta_0 \) and only the lower plate has any effect on the bead. Thus, even when the bottom and the top plates are far away from the BP we get \( \eta_{x,y,z} = \eta_0 \).

The relation (16) takes into account independent presence of the bottom and the top plate on the damping coefficient of the BP without considering any interaction. Imagine that, only the bottom plate is present and the damping coefficient is modified due only to its presence, such that, \( \eta_{x,y,z} = \eta_0 + \Delta \eta^b(z) \), where \( \Delta \eta^b(z) \) is the modification of damping due to the presence of bottom plate on top of what it is there in the bulk. Similarly, when one takes into account the presence of the top plate, whose hydrodynamic effect is not going to interfere with that produced by the bottom plate, there would also be an increase in the damping by an amount \( \Delta \eta^u(z) \) on top of what the bottom plate has produced. Therefore, the new damping coefficient considering the presence of both the plates is

\[
\eta_{x,y,z} = \eta_0 + \Delta \eta^b(z) + \Delta \eta^u(z)
\]

\[
= [\eta_0 + \Delta \eta^b(z)] + [\eta_0 + \Delta \eta^u(z)] - \eta_0
\]

\[
= \eta_{x,y,z}^b + \eta_{x,y,z}^u - \eta_0.
\]

We have found this expression (16) to work quite well in taking into account the hydrodynamic effect due to both the plates.
TABLE I: Table contains data used to plot all the graphs. Experimental data is taken from [38].

### D. Comparison of the BD with MBD

We compare theoretically obtained height–averaged horizontal diffusivity $\langle D_{||} \rangle^{B/MB}$ with the experimental results $D_{||}^{(expt)}$ of [38]. We use two different distributions, the BD and MBD, to get the height–averaged (z–averaged) horizontal diffusivity in the following way

\[
\langle D_{||} \rangle^{B} = \int_{r+\epsilon}^{t-(r+\epsilon)} D_h(z)P_B(z)dz, \tag{17}
\]

\[
\langle D_{||} \rangle^{MB} = \int_{r+\epsilon}^{t-(r+\epsilon)} D_h(z)P_{MB}(z)dz. \tag{18}
\]

The distributions are

\[
P_B = N_B \exp(-z/L), \tag{19}
\]

\[
P_{MB} = N_{MB}D_{\perp}(z)^{-1}\exp(-z/L), \tag{20}
\]

where $N_B$ and $N_{MB}$ are the normalization constants for the BD and MBD, respectively, evaluated exactly over the same lower/upper limits for a particular bead. We implement a cut–off distance $\epsilon = 10^{-3}\mu m$ to avoid the divergence appearing in the MBD due to vanishing of $D_{\perp}(z)$ at $z = r$ and $z = t - r$. Numerical integration being presented here is a left–Riemann–sum with bin–width $10^{-3}\mu m$. Because of the presence of divergence, we also have checked the parity between left and right Riemann–sum and that is excellent for the considered bin–size.

It is important to note that, for a matching of the experimental results with the theoretical ones (17) and (18), we need to find out the theoretical values of the average diffusion coefficients for each individual particle because that corresponds to different experimental conditions. The limitation of parameter $\gamma$ is its distribution dependence. We, therefore, need a parameter which is distribution independent such that we can overlay theoretical results on the same plot.

In the Fig.2, we compare the experimental results with the $\langle D_{||} \rangle^{B/MB}$, where we use the parameter $tL/100$. Normalization of this parameter by a factor of 1/100 is done in order to keep the horizontal scale similar to that in Fig.1 for the ease of comparison. The $\langle D_{||} \rangle^{B/MB}$ have been computed for the Fig.2 using $\eta_{x,y,z}$ as given in relation (16), i.e., we take into account the hydrodynamic effect due both, to the top and bottom, confining plates. In this figure, we have plotted $\langle D_{||} \rangle^{B}$ by dots and $\langle D_{||} \rangle^{MB}$ by circles. We have drawn a cubic spline (continuous line, smoothing factor 0.1) to only the $\langle D_{||} \rangle^{MB}$ and not for $\langle D_{||} \rangle^{B}$ because the comparison is clear even without that extra curve.
FIG. 2: The figure shows a comparison of $\langle D_{||}\rangle^{B/MB}/D_0$ with the experimental results $D_{||}/D_0$. In the computation of $\langle D_{||}\rangle^{B/MB}/D_0$, effects of both upper and lower plates are taken into account in accordance with relation [8]. The continuous line is a cubic spline of smoothing factor 0.1 to the data corresponding to MBD.

This figure shows that, $\langle D_{||}\rangle^{MB}$ and $\langle D_{||}\rangle^{B}$ do not deviate much for very heavy particles. The average diffusivity of these do not depend too much on their vertical excursion which is rather limited by the weight. On other hand, the experimental trend set by relatively lighter particles which undergo much vertical excursion is clearly better captured by the MBD. This particularly includes particles which are heavy but also having sufficient vertical excursion and are plotted within the range of parameter $tL/100 \leq 1$. The deviation of results corresponding to the BD from MBD is the most in this region and the MBD better captures the trend of the experimental results.

To understand how important it is to take into account the presence of both the plates in computing the average horizontal diffusivity, we have also computed the $\langle D_{||}\rangle^{B/MB}$ taking into account $\eta_{x,y,z}$ due only to the lower plate. We have plotted corresponding data by the symbol of star for the $\langle D_{||}\rangle^{MB}$ and sold triangle for $\langle D_{||}\rangle^{B}$ in Fig.3 on top of what is there in Fig.2. Obviously, the removal of upper plate would lead to a higher theoretical count for the average diffusivity and that is evident from the Fig.3. Dashed line in the Fig.3 is cubic spline corresponding to the star symbols. Fig.3 clearly indicates that, taking into account the presence of both confining plates or the lower one alone has substantial effect on the theoretical results.

It may appear from Fig.2 that, the MBD is not matching the larger diffusivity region as much as the BD does. Note
that, the error bars in the higher diffusivity region are larger due to limitations in the averaging process over the experimental trajectories mentioned in [38]. Let us look at the data of higher diffusivity (near bulk) more closely. For example, consider the sample number 18 in Table 1, which is the third experimental data–point in the plots from right hand side end. It is clearly an over count. This particle has a bead diameter 1 μm which is the same as bead of the sample number 19 and both have the same density. Where, the sample number 18 has a width \( t = 12 \mu m \), that of the sample number 19 is 25. Given this, the \( D_P / D_0 \) of sample number 18 should be smaller than that of the 19. However, that is not the experimental result as shown in Table 1. Similarly, if one compares the experimental value of \( D_{||}/D_0 \) of sample number 17 with that of the 19, one would find that the experimental value is larger (quite close to that of sample number 19) than what it should be given bigger diameter of the bead number 17. Experimental data in Table 1, this way, reveals that there apparently exists some bias towards over counting the diffusivity of lighter particles. This might be related to the problem of focussing on lighter particles which undergo much more vertical excursion than the heavier ones. After all, the experiment was done about 30 years ago when depth resolved particle tracking was not efficient.

The MBD (Itô–distribution) is able to match the trend of average diffusivity observed in the experiment better than BD which over–counts most of the samples. Expressions of the BD and MBD can simply explain this. In the MBD, there is a transfer of weight toward the region of relatively smaller \( D_{||}(z) \), i.e., toward the vicinity of confining plates where \( D_{||}(z) \) is also smaller in value. This is the reason, MBD accounts for the experimental average in a much better way, as compared to what is given by the BD, for the beads those experience substantial hydrodynamic effect due to the proximity of confining plates.

In [38], to fit the experimental data with the BD, a doubly averaged horizontal diffusivity \( D_{||} = \int_{0}^{t} D'_{||}(z) P_B(z)dz \) is used, where \( D'_{||}(z) = \int_{z-\delta}^{z+\delta} d\zeta D(\zeta) P_B^0(\zeta) d\zeta \) which is a local average of \( D_{||}(z) \) over a vertical window of 2\( \delta \) using a normalized BD, \( P^0_B(\zeta) \) within this interval. Apparently, this \( D_{||} = \int_{0}^{t} D'_{||}(z) P_B(z)dz \) could fit the experimental result where \( D_{||} = \int_{0}^{t} D_{||}(z) P_B(z)dz \) could not. In the computation of \( D'_{||}(z) \), due to the nature of gravitational field, there is a transfer of weight in \( P_B^0(\zeta) \) from the upper \( \delta \)–interval to the lower \( \delta \)–region. However, the lower \( \delta \)–interval of the local window, mostly being closer to the lower plate, observes a lower value of diffusivity compared to that in the upper \( \delta \)–window at each \( z \) and that reduces \( D'_{||}(z) \) in comparison to the theoretical \( D_{||}(z) \). It gives a lower count in the double average scheme using the BD as compared to \( D_{||} = \int_{0}^{t} D_{||}(z) P_B(z)dz \) which, in general, should be the theoretical average. This effect would be even more pronounced if one does not take into account the presence of the upper plate in \( \eta_{x,y,z} \). This might also be the reason for the observation in [38] that the upper plate has negligible effect on the diffusivity of beads. However, in Fig.3, we see that the effect of upper plate could be substantial in certain cases depending upon the diameter of sample and nature of a bead.

### IV. DISCUSSION

We have given here a physical interpretation of Itô–process from Gibbs measure and have identified the Hamiltonian of system at small \( m \) limit. To our knowledge, such an attempt to understand the Itô–process for coordinate dependent diffusion is novel and, probably, the absence of it has been the reason for not considering the Itô–distribution for equilibrium. Knowing the correct distribution of a non–linear stochastic process is of paramount importance because the statistics of all near–equilibrium systems (linear response regime) with coordinate–dependent diffusion will follow this distribution. Itô–distribution could be a crucial ingredient, so far not taken into account, to understand structural transitions in complex molecules of biological systems and a host of other processes.

Experimental results of [38] is very reliable because it has used ultra–pure water as the fluid. Use of ultra–pure water and other experimental cares taken to keep the fluid pure (or doing the experiment within time when the fluid remains contaminant–free) has kept the potential term for the Boltzmann factor to be in its simplest form. Practically, no amount of free ion was presumably present in the fluid helping avoid the presence of any Debye-Huckel term. Moreover, this is the experiment which has indicated limitation of BD about 30 years ago as reported in [38]. A similar experiment using ultra–pure water as solvent can conclusively prove the MBD to be equilibrium distribution.
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[27] A. Bhattacharyay, Generalization of stokes–einstein relation to coordinate dependent damping and diffusivity: an apparent


