CORRELATION PROPERTIES OF THE THERMAL NOISE IN FLUIDS

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1. Introduction

In this contribution we deal with the correlation properties of the random force driving the motion of Brownian particles in fluids. It is shown that when the often used properties of this force in incompressible fluids are assumed [1,2], this results in an unexpected motion of the particles, which will be of super-diffusive character. Since normal diffusion should take place, which is an undoubted experimental fact [3], this contradiction needs to be resolved. We show that obtaining the expected Einstein diffusion at long times requires that the correlation function of the random force at the time t and the particle velocity at previous moments of time must be nonzero. This apparent paradox is explained. We also consider the "color" of the thermal noise, for the first time probed experimentally in [4], and correct the interpretation of these measurements. The time correlation function of the thermal random force is calculated. Its properties are shown to significantly differ from those found in the literature [1,2,4].

2. Properties of thermal random force in incompressible fluids

It has been known for a long time that the Langevin equation describing the Brownian motion of particles in fluids is valid only under very limited conditions [1-3]. When the density of the particles is comparable to that of the fluid, the standard Einstein-Langevin theory should be significantly changed: the Stokes force modeling the resistance against the particle motion must be replaced with a force that reflects the "history" of the particle dynamics. Within the linearized non-stationary Navier-Stokes hydrodynamics for incompressible fluids, an exact expression for this force can be obtained [5]. Using it, the Langevin equation for the particles moving in the direction x with the velocity $\upsilon = \mathrm{d}x/\mathrm{d}t$ has been generalized to the form [1,2,6]

$$M\dot{\upsilon}(t)+\gamma\upsilon(t)+\int_0^t \Gamma(t-t')\dot{\upsilon}(t')\,\mathrm{d}t' = F+\zeta(t). \qquad (1)$$

Here, the noise force $\zeta(t)$ with zero mean drives the particles of mass M_p ($M = M_p + M_s/2$ with M_s being the mass of the solvent displaced by the particle), $\gamma = 6\pi\eta R$ is the Stokes friction coefficient for spherical particles with radius R, ρ is the density, η the dynamic viscosity of the solvent, and F stays for a regular external force. The random force ζ is, due to the fluctuation dissipation theorem [7], connected to the dissipative properties of the system, described by the Stokes term and the convolution integral with the kernel $\Gamma(t) = \gamma(\tau_R/\pi t)^{1/2}$. The vorticity time $\tau_R = R^2\rho/\eta$ characterizes the loss of the hydrodynamic memory in the particle motion. The usual Brownian relaxation time $\tau = M/\gamma$ is connected to τ_R by the relation $\tau_R/\tau = 9\rho/(2\rho_p + \rho)$, where ρ_p is the density of the particle.

Now our aim is to calculate from Eq.(1) the velocity autocorrelation function (VAF) of the free particle, $\phi(t) = \langle \upsilon(t)\upsilon(0)\rangle$, and its mean square displacement (MSD) $X(t) = \langle \Delta x^2(t)\rangle = \langle [x(t) - x(0)]^2\rangle$. The brackets $\langle \ldots \rangle$ stay for statistical averaging. Assuming the equilibrium between the particle and the solvent, in agreement with the equipartition theorem for the particle of mass M the condition $\phi(0) = k_BT/M$ is used for the VAF. Then, multiplying Eq.(1) by $\upsilon(0)$ and assuming that $\langle \zeta(t)\upsilon(0)\rangle = 0$, after the average one obtains

$$M\dot{\phi} + \gamma\phi + \int_0^t \Gamma(t-t')\dot{\phi}(t')\,\mathrm{d}t' = 0 \qquad (2)$$

With the help of the Laplace transformation $\tilde{\phi}(s) = \Lambda\{\phi(t)\}$, Eq.(2) is easily solved in terms of the complementary error function. We do not write here the full solution, just show its asymptotes for short and long times: $\phi(t) \approx (k_BT/M)(1 - t/\tau + \ldots)$ at $t \to 0$, and $\phi(t) \approx (k_BT/M)(\tau_R/\pi t)^{1/2}[1 - (\tau_R/2t)(1 - 2\tau/\tau_R) + \ldots]$ as $t \to \infty$. Representing the distance a particle moves in time as an integral of its velocity, $x(t) - x(0) = \int_0^t \upsilon(s)\,\mathrm{d}s$, the MSD is obtained as $X(t) = 2\int_0^t (t-s)\phi(s)\,\mathrm{d}s$ [8]. At short times it shows the ballistic behavior, $X(t \to 0) \sim k_BTt^2/M$, confirmed experimentally (e.g., in [4)]. At $t \to \infty$, the main term is $X(t) \approx (8k_BT/3M)(\tau_R t^3/\pi)^{1/2}$. Since $X(t \to \infty) \sim t^{3/2}$, the solution has a super-diffusive character.

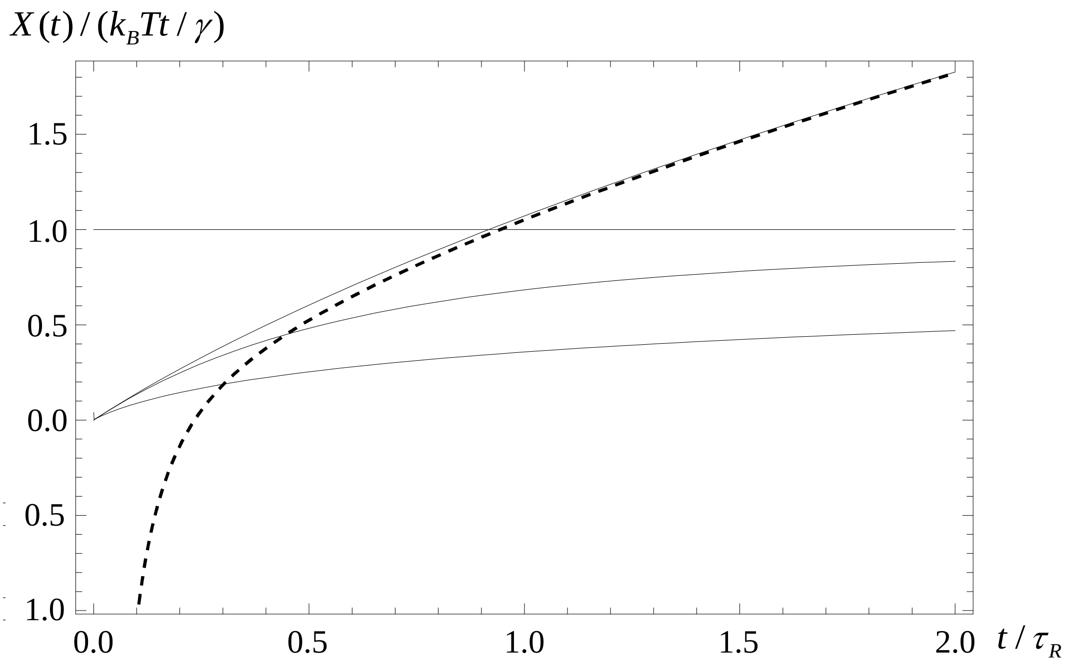

Fig.1: *Mean square displacement normalized to the Einstein result for resin particles (with R = 1.25 μm and the density $1.5\cdot10^3$ kg$\cdot$m^{-3}) in water at room temperature ($\eta = 10^{-3}$ Pa$\cdot$s, $\rho = 10^3$ kg$\cdot$m^{-3}, $\tau_R = 1.56\cdot10^{-6}$ s, $\tau = 0.52\cdot10^{-6}$ s). The full line corresponds to super-diffusion, with the dashed line being its long-time limit, see the text. The lower full lines are for the standard Langevin theory [3] and the correct hydrodynamic solution of Eq.(1).*

Of course, this unexpected result is not correct. It contradicts both the Einstein-Langevin theory and numerous experiments. The arising problem can be resolved as follows. If we assume that the studied process is in thermodynamic equilibrium, the initial value $\upsilon(0)$ (for which we assumed that the equipartition holds) should be the result of the long time memory in the system. Then in Eq.(1) the lower limit of integration should be $-\infty$ and the random force $\zeta(t)$ must be replaced by $\eta(t)$ that obeys the principle of causality, i.e., $\langle \eta(t)\upsilon(0)\rangle = 0$. Alternatively, one can use the Langevin equation in the form (1), but as distinct from the works [1,2,6], the force $\zeta(t)$ must have a nonzero correlator $\langle\zeta(t)\upsilon(0)\rangle = Z(t)$. If one requires that the Einstein's diffusion takes place at long times, the only possibility is that $Z(t) = -k_B T\tau \times(\tau_R/\pi t)^{1/2}$. Equation (2) with such $Z(t)$ on the right-hand side instead of 0 possesses the correct solution for the VAF and MSD that can be obtained also in a different way, without an explicit use of the correlation properties of the thermal noise [8]. For short times we have the same ballistic behavior of the particle as above, but at long times the MSD will be $X(t) = 2D[t - 2(\tau_R t/\pi)^{1/2} + \tau_R - \tau + ...]$, where $D = k_B T\tau/M$ is the usual Einstein diffusion coefficient. We can conclude that the "fundamental hypothesis" for Eq.(1), according to which $\langle\zeta(t)\upsilon(0)\rangle = 0$, must be abandoned.

Another important property of the thermal noise is its "color", or the time correlation function of the noise force itself. Although the thermal force in the Langevin equation is a physical reality and should be observable [7], its color has been directly measured only very recently in the work by Franosch et al. [4]. Combining strong optical trapping with high-resolution interferometric detection, the correlations in thermal noise became directly accessible by calculating the positional autocorrelation function from the recorded position fluctuations of the particle trapped in a harmonic potential. Analyzing the hydrodynamic Langevin equation (1) with the external force $F = -Kx(t)$, the correlator $\langle\zeta(t)\zeta(0)\rangle$ has been determined as $\langle\zeta(t)\zeta(0)\rangle \approx K^2\langle x(t)x(0)\rangle$, where K is the stiffness constant of the trap. It is easy to see that this approach is flawed. While at long times (low frequencies) the particle inertia can be neglected, so that Eq.(1) is reduced to $Kx(t) \approx \zeta(t)$, at $t \to 0$ the force term $Kx(t)$ is less important than the inertia term, the memory integral, and the frictional force $\gamma\upsilon$. The approximation $Kx(0) \approx \zeta(0)$ thus does not hold. Here we proceed in a different way. Since within the linear response theory the external force does not affect the properties of the thermal force [7], the correlation function $N(t) = \langle\zeta(t)\zeta(0)\rangle$ can be obtained omitting in Eq.(1) the term $Kx(t)$. Multiplying this equation by $\zeta(0)$ and averaging, we find in the Laplace transformation for the studied stationary process

$$\tilde{N}(s) = \gamma^2\tilde{\phi}(s) - \left[M^2 s + Ms\tilde{\Gamma}(s) - \gamma\tilde{\Gamma}(s)\right]\left[s\tilde{\phi}(s) - \phi(0)\right], \qquad (3)$$

where $\tilde{\phi}(s)$ is the transform of the VAF,

$$\tilde{\phi}(s) = \frac{k_B T}{M}\frac{1}{s + (\tau_R s)^{1/2}\tau^{-1} + \tau^{-1}}. \qquad (4)$$

Using Eq.(4), we find

$$\tilde{N}(s)/\phi(0) = \gamma M + \tilde{\Gamma}(s)\left[Ms - \gamma\right]. \qquad (5)$$

The inverse transform of this equation is

$$N(t) = k_B T\gamma\left[\delta(t) - \frac{1}{\tau}\sqrt{\frac{\tau_R}{\pi t}}\theta(t) - \frac{1}{2}\sqrt{\frac{\tau_R}{\pi t^3}}\theta(t)\right], \qquad (6)$$

where $\delta(t)$ and $\theta(t)$ are the Dirac delta and Heaviside function, respectively. This expression is similar to that found in [1,4], $\langle\zeta(t)\zeta(0)\rangle = -0.5 k_B T\gamma(\tau_R / \pi t^3)^{1/2}$, except the second term in square brackets that is missing there. In our solution at $t > 0$ we have the correlator $\langle\zeta(t)\zeta(0)\rangle = -k_B T\gamma(\tau_R / \pi t)^{1/2}(1/\tau + 1/2t)$. The time correlation function of the thermal noise in incompressible fluids thus at long times approaches zero as $\sim t^{-1/2}$ instead of $t^{-3/2}$ found in [1,4].

3. Conclusion

This work deals with the properties of the thermal noise driving the Brownian particles. Using an effective method of solving linear generalized Langevin equations [8,9], we have shown that the expected Einstein diffusion can be obtained from the hydrodynamic Langevin equation in the form (1) only in the case when the thermal force $\zeta(t)$ at $t > 0$ correlates with the velocity of the particle at the time $t = 0$. This is in contradiction with the "fundamental hypothesis" (according to which these quantities are uncorrelated) used in a number of papers dealing with the normal and generalized Langevin equation [1,2,4,6]. We have found the corresponding correlator $\langle\zeta(t)\upsilon(0)\rangle$. Note that the Einstein diffusion at long times is also obtained when another basic theorem from the linear response theory is applied: this theorem joins the mobility of the particle and its velocity autocorrelation function. Finally, we discussed the question of the color of the thermal noise. It was claimed in the recent work [4] that this color was experimentally measured through the correlation function of the particle positions. We have shown that the interpretation of these experiments should be corrected and calculated the time correlation function of the thermal noise within the hydrodynamic theory of the Brownian motion. The difference between our results and those found in previous works [1, 2] is significant. Since in the linear approximation the thermal force is not influenced by the external forces, the obtained results can be used in consistent solution of the problem of Brownian motion in a harmonic trap, which is related to numerous experiments on colloidal systems.

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