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Statistical Properties of Thermal Noise Driving the Brownian Particles in Fluids

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Abstract. In several recent works high-resolution interferometric detection allowed to study the Brownian motion of optically trapped microparticles in air and fluids. The observed positional fluctuations of the particles are well described by the generalized Langevin equation with the Boussinesq-Basset "history force" instead of the Stokes friction, which is valid only for the steady motion. Recently, also the time correlation function of the thermal random force F_{th} driving the Brownian particles through collisions with the surrounding molecules has been measured. In the present contribution we propose a method to describe the statistical properties of F_{th} in incompressible fluids. Our calculations show that the time decay of the correlator $\langle F_{\mathrm{th}}(t)F_{\mathrm{th}}(0)\rangle$ is significantly slower than that found in the literature. It is also shown how the "color" of the thermal noise can be determined from the measured positions of the Brownian particles.

1 Introduction

Random processes in various fields of science are often described by phenomenological equations of motion containing stochastic forces, the best known example being the Langevin equation (LE), first designed to describe the Brownian motion (BM) of particles [1]. However, as it is known for a long time theoretically [2–5] and reported in experiments (see, *e.g.*, the review [6]), the LE fails to describe the motion of the Brownian particles when their density is comparable to that of the surrounding. Beginning with [7], the BM in fluids was successfully studied using the high-resolution interferometry of optically trapped particles [8–10]. These experiments are in excellent agreement with the prediction for the mean square displacement of the particle and related correlation functions within the hydrodynamic theory of the BM of particles confined in a harmonic potential well [4]. The experimental access to short timescales [10] allowed also obtaining the time correlation function $\langle F_{\mathrm{th}}(t)F_{\mathrm{th}}(0)\rangle$ of the thermal random force $F_{\mathrm{th}}(t)$, resulting from the collisions with the surrounding molecules and thus responsible for the BM of the particles. The work [10] can be considered as the first work where the "color" of the thermal noise has been measured. The method of calculation of $\langle F_{\mathrm{th}}(t)F_{\mathrm{th}}(0)\rangle$ from the measured positional fluctuations of the particles proposed in [10, 11] leads

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to a dependence $\langle F_{\rm th}(t)F_{\rm th}(0)\rangle \sim t^{-3/2}$. The discussion done below reveals shortcomings of this method and gives two different ways to calculate the function $\langle F_{\rm th}(t)F_{\rm th}(0)\rangle$. In the frame of the linear hydrodynamic theory of the BM in incompressible fluids our calculations are exact. At long times the decay of $\langle F_{\rm th}(t)F_{\rm th}(0)\rangle$ is much slower than previously assumed in [6, 10–12].

2 Time correlations of the thermal noise

In the classical LE the resistance force against the motion of the Brownian particles is the Stokes friction force proportional to the particle velocity. In a more general hydrodynamic theory of the BM [2] the Stokes force is replaced by the Boussinesq force [13], derived from the linearized Navier-Stokes and continuity equations for incompressible fluids. This force describes hydrodynamic interactions of a spherical tracer with the surrounding fluid [14]. These interactions appear at short time scales and, as distinct from the more familiar Kubo's generalization of the LE [15], the memory integral contains the acceleration of the Brownian particle instead of its velocity. The LE for the velocity $\upsilon(t) = \mathrm{d}x/\mathrm{d}t$ of Brownian particles then has the form

$$m\dot{\upsilon}\,(t) + \gamma\upsilon\,(t) + \int_{t_0}^{t} \Gamma\,(t-t')\dot{\upsilon}\,(t')\,\mathrm{d}t' = F_{\rm th}\,(t)\,, \tag{1}$$

where $\Gamma(t) = \gamma(\tau_{\rm f}/\pi t)^{1/2}$ with $\tau_{\rm f} = R^2\rho_{\rm f}/\eta$, R is the radius of the particle, $\rho_{\rm f}$ is the fluid density and η its viscosity, $\gamma = 6\pi\eta R$ is the Stokes friction coefficient, and $m = m_{\rm p} + m_{\rm f}/2$, with $m_{\rm f}$ being the mass of the fluid displaced by the particle of mass $m_{\rm p}$ (we use the same notation as in [10]). The particle is assumed to be in thermal equilibrium with the liquid. The time t_0 denotes an initial moment infinitely remote from t. When the particle is in an external harmonic field, the force $-Kx(t)$, where $x(t)$ is the particle displacement from the trap center, should be added in the right side of (1). In the traditional LE the thermal noise force $F_{\rm th}(t)$ is white. This is not the case here since, due to the fluctuation-dissipation theorem [15], the values of $F_{\rm th}(t)$ at different times correlate. The authors of [10] have accessed the correlations in the colored $F_{\rm th}(t)$ by recording the positions of the particle and calculating the autocorrelation function $\langle x(t)x(0)\rangle$. It was assumed that at long times the trapping force dominates over friction. Ignoring the particle inertia, the LE was thus reduced to $Kx(t) \approx F_{\rm th}(t)$. Then it was assumed that $\langle F_{\rm th}(t)F_{\rm th}(0)\rangle \approx K^2\langle x(t)x(0)\rangle$. However, this requires that $Kx(0) \approx F_{\rm th}(0)$ also holds, which is not true; in fact, at $t \to 0$, $Kx(t)$ is less important than other terms in the LE. Here we show that the calculation of $\langle F_{\rm th}(t)F_{\rm th}(0)\rangle$ is possible without these approximations.

Within the linear theory, the properties of $F_{\rm th}(t)$ do not depend on the external force [15]. To find $\langle F_{\rm th}(t)F_{\rm th}(0)\rangle$, it is thus possible to use the LE without the term $Kx(t)$ and proceed as follows. One can rewrite Eq. (1) for $\upsilon(t_0+t), t > 0$, transform the integral to $\int_0^t$, multiply this equation by $F_{\rm th}(t_0) = m\dot{\upsilon}(t_0) + \gamma\upsilon(t_0)$, and statistically average. For stationary processes $\langle\dot{\upsilon}(t_0)\upsilon(t_0+t)\rangle = -\langle\upsilon\,(t_0)\,\dot{\upsilon}\,(t_0+t)\rangle = -\dot{\phi}\,(t)$ and all the terms in the resulting equation for $\langle F_{\rm th}(t_0)F_{\rm th}(t_0+t)\rangle$ can be expressed through the velocity autocorrelation function $\phi(t) = \langle\upsilon(t)\upsilon(0)\rangle$, *e.g.*, $\langle\dot{\upsilon}(t_0)\dot{\upsilon}(t_0+t)\rangle = (\mathrm{d}/\mathrm{d}t)\,\langle\dot{\upsilon}(t_0)\upsilon(t_0+t)\rangle = -\ddot{\phi}(t)$. In the Laplace transformation we obtain

$$\mathcal{L}\{\langle F_{\rm th}\,(t)\,F_{\rm th}\,(0)\rangle\} = \gamma^2\tilde{\phi}\,(s) - \left[m^2 s + ms\tilde{\Gamma}\,(s) - \gamma\,\tilde{\Gamma}\,(s)\right]\left[s\tilde{\phi}\,(s) - \phi\,(0)\right]. \tag{2}$$

Then, using $\dot{\phi}(0) = 0$ and $\phi(0) = k_BT/m$ (the equipartition theorem), the Laplace-transformed equation for $\tilde{\phi}(s) = \mathcal{L}\{\phi(t)\}$ can be found from (1). In the theory of the hydrodynamic BM [3, 16–18]

$$\tilde{\phi}(s) = k_BT\left\{\gamma + s\left[m + \tilde{\Gamma}(s)\right]\right\}^{-1}, \tag{3}$$

so that Eq. (2) is transformed to

$$\mathcal{L}\{\langle F_{\mathrm{th}}(t)\, F_{\mathrm{th}}(0)\rangle\} = k_B T\left[\gamma + \tilde{\Gamma}(s)\left(s - \frac{1}{\tau}\right)\right], \tag{4}$$

where $\tilde{\Gamma}(s) = \gamma(\tau_{\mathrm{f}}/s)^{1/2}$ and $\tau = m/\gamma$. Consequently, the inverse transform for $t > 0$ reads [19]

$$\langle F_{\mathrm{th}}(t)\, F_{\mathrm{th}}(0)\rangle = -k_B T\gamma\left(\frac{\tau_{\mathrm{f}}}{\pi t}\right)^{1/2}\left(\frac{1}{\tau} + \frac{1}{2t}\right). \tag{5}$$

Only the term $\sim t^{-3/2}$ has been reported in the literature [6, 10–12]. Note that the additional term is longer-lived. This is essential in the determination of $\langle F_{\mathrm{th}}(t)\, F_{\mathrm{th}}(0)\rangle$ from the measurements of the particle positions. For a detailed discussion of the shortcomings in the derivation of $\langle F_{\mathrm{th}}(t)\, F_{\mathrm{th}}(0)\rangle$, see [20]. Here we add a few short remarks. First, instead of Eq. (1) (with $t_0 = -\infty$), one can use the equation

$$m\dot{\upsilon}(t) + \gamma\upsilon(t) + \int_0^t \Gamma(t - t')\dot{\upsilon}(t')\,\mathrm{d}t' = F + \zeta(t), \tag{6}$$

where $\zeta(t) = F_{\mathrm{th}}(t) - \int_{-\infty}^{0} \Gamma(-t')\,\dot{\upsilon}(t')\,\mathrm{d}t'$ is a new random force and F is an external force. One must take into account that whereas $\langle F_{\mathrm{th}}(t)\,\upsilon(0)\rangle = 0$ due to causality, now the correct solution can be obtained only assuming that $Z(t) = \langle\zeta(t)\,\upsilon(0)\rangle = (-k_B T\gamma/m)(\tau_{\mathrm{f}}/\pi t)^{1/2}$, *i.e.*, the force $\zeta(t)$ and the velocity $\upsilon(0)$ correlate at $t > 0$ [20] (note that this equality is implicitly required in Ref. [21] since only in this case Eq. (9) of that paper is valid). This is in disagreement with some previous results from the literature [22], where the condition $Z(t) = 0$ is considered as a “fundamental hypothesis” for solving the LE (6). Our result for the correlator $Z(t)$ can be proven also coming from the basic theorem of the linear response theory (a generalization of the first fluctuation dissipation theorem) [15]. In the Laplace transformation it reads

$$\tilde{\phi}(s) = k_B T\tilde{\mu}(s), \tag{7}$$

where $\mu(t)$ is the admittance (or mobility) of the particle that determines the drift (mean) velocity under the influence of an external force F. Using the solution of Eq. (6) with $F = 0$,

$$\tilde{\phi}(s) = \tilde{\mu}(s)\left\{\left[m + \tilde{\Gamma}(s)\right]\phi(0) + \tilde{Z}(s)\right\}, \tag{8}$$

and Eq. (7), we find $\tilde{Z}(s) = -k_B T\tilde{\Gamma}(s)/m$, which is the Laplace transformation of the above obtained $Z(t)$. The correlation function for $\zeta(t)$ can be obtained in a similar way as above and it is the same as for the “true” thermal force $F_{\mathrm{th}}(t)$. One can see it from the relation between $F_{\mathrm{th}}(t)$ and $\zeta(t)$ below Eq. (6), due to which $\langle\zeta(t)\zeta(0)\rangle = \langle F_{\mathrm{th}}(t)F_{\mathrm{th}}(0)\rangle + C$. The time-independent term C is zero since at $t \to \infty$ both the correlators must converge to zero.

3 Conclusions

Many years ago Kubo [15] pointed out that the thermal noise present in the Langevin equation is a physical reality and should be observable. The experiments with the aim to observe it were realized only very recently [10, 12] on Brownian particles in optical traps. However, the correlation function of the thermal force is not measured directly; it is extracted from the data on the particle positional autocorrelation function (PAF). Although the PAF in the cited papers is correct within the hydrodynamic theory used also in the present work, its relation to $\langle F_{\text{th}}(t) F_{\text{th}}(0)\rangle$ is improper. Here we have proposed an interpretation of these measurements that differs from the original one. Our results were obtained by two methods: directly from the hydrodynamic Langevin equation and using a basic formula from the linear response theory that joins the mobility of the particle and its velocity autocorrelation function. Whereas in [10] the correlation function of the noise is proportional to the PAF, according to our result (5) and the PAF long-time asymptote (experimentally confirmed in [10]), $\langle x(t)x(0)\rangle = k_B T/K - X(t)/2 \approx -k_B T\gamma(\tau_f/4\pi t^3)^{1/2}/K^2$ [4, 10, 20], where $X(t)$ is the mean square displacement, the correlator of the thermal force that follows from the experiments [10] at $t \gg \tau_f$ is

$$\langle F_{\text{th}}(t) F_{\text{th}}(0)\rangle \approx K^2 \left(1 + \frac{2t}{\tau}\right) \langle x(t)\, x(0)\rangle . \quad (9)$$

It significantly differs from the one obtained in Ref. [10], $\langle F_{\text{th}}(t)F_{\text{th}}(0)\rangle \approx K^2\langle x(t)x(0)\rangle$, the unsoundness of which from the physical point of view has been demonstrated above. The proposed description of the Brownian motion can be used to interpret numerous experiments on colloidal systems in external fields.

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References

[1] P. Langevin, P. C. R. Acad. Sci. (Paris) **146**, 530 (1908)
[2] V. Vladimirsky, Ya. Terletzky, Zh. Eksp. Teor. Fiz. **15**, 258 (1945)
[3] E. J. Hinch, Fluid Mech. **72**, 499 (1975)
[4] H. J. H. Clercx, P. P. J. M. Schram, Phys. Rev. A **46**, 1942 (1992)
[5] V. Lisy, J. Tothova, arXiv:cond-mat/0410222 [cond-mat.stat-mech]
[6] T. Li, M. G. Raizen, Ann. Phys. (Berlin) **525**, 281 (2013)
[7] B. Lukić *et al.*, Phys. Rev. Lett. **95**, 160601 (2005)
[8] B. Lukić *et al.*, Phys. Rev.E **76**, 011112 (2007)
[9] R. Huang *et al.*, Nature Phys. **7**, 576 (2011)
[10] Th. Franosch *et al.*, Nature **478**, 85 (2011)
[11] K. Berg-Sørensen, H. Flyvbjerg, New J. Phys. **7**, 2 (2005)
[12] A. Jannasch, A. Mahamdeh, E. Schäffer, Phys. Rev. Lett. **107**, 228301 (2011)
[13] J. Boussinesq, P. C. R. Acad. Sci. (Paris) **100**, 935 (1885)
[14] D. S. Grebenkov, M. Vahabi, Phys. Rev. E **89**, 012130 (2014)
[15] R. Kubo, Rep. Prog. Phys. **29**, 255 (1966)
[16] Karmeshu, J. Phys. Soc. Japan **34**, 1467 (1973)
[17] J. Tothova *et al.*, Eur. J. Phys. **32**, 645 (2011)
[18] J. Tothova *et al.*, Eur. J. Phys. **32**, L47 (2011)
[19] M. Abramowitz, I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, DC, 1964)
[20] J. Tothova, L. Glod, V. Lisy, Int. J. Thermophys. **34**, 629 (2013)
[21] A. Widow, Phys. Rev. A **3**, 1394 (1971)
[22] F. Mainardi, P. Pironi, Extracta Mathematicae **10**, 140 (1996)