Journal of Statistical Mechanics: Theory and Experiment
An IOP and SISSA journal

Fluctuations of non-conservative systems

Dino Leporini[1,2] **and Roberto Mauri**[3]

[1] Department of Physics 'Enrico Fermi', Università di Pisa, I-56127 Pisa, Italy
[2] SOFT-INFM-CNR, P.zza A. Moro 2, I-00185, Roma, Italy
[3] Department of Chemical Engineering, Industrial Chemistry and Material Science, Università di Pisa, I-56126 Pisa, Italy
E-mail: dino.leporini@df.unipi.it and r.mauri@ing.unipi.it

Received 3 January 2007
Accepted 13 February 2007
Published 1 March 2007

Online at stacks.iop.org/JSTAT/2007/P03002
doi:10.1088/1742-5468/2007/03/P03002

Abstract. When a non-conservative system fluctuates around its steady configuration, in general, neither equipartition nor the fluctuation–dissipation theorem are satisfied. Using a path integral approach, we show that in this case the probability distribution is determined in terms of the energy dissipated along the minimum path. The latter is the path of minimum energy dissipation of a fictitious, unit mass particle, moving with constant energy under the influence of an electric and a magnetic field. In addition, the instantaneous speed of this particle equals the mean backward velocity of the Brownian particle. At the end, a Boltzmann-like probability distribution is obtained, which allows us to define an effective temperature kernel. In particular, when the forces applied to the particle are linearly dependent on the distance from the origin, the effective temperature turns out to be the sum between an isotropic and an antisymmetric tensor, which allows us to generalize the fluctuation–dissipation theorem.

Keywords: driven diffusive systems (theory), exact results, stochastic particle dynamics (theory), transport processes/heat transfer (theory)

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1. Introduction

In classical thermodynamics, an isolated system tends to assume its equilibrium configuration which, according to the second law, is unique and corresponds to the state in which the energy functional is minimized [1]. In fact, any classical thermodynamic system is assumed to have an infinite number of degrees of freedom and, consequently, its stable equilibrium state is infinitely more probable than any other state.

On the other hand, finite systems fluctuate, as all configurations around the equilibrium state have a finite probability to occur. Since, according to the equipartition theorem (EPT), each degree of freedom gives a constant contribution to the total free energy of the system, this probability is the Boltzmann distribution, $C\exp[-\phi(\mathbf{x})/kT]$, where $\phi(\mathbf{x})$ is the energy of the state $\mathbf{x}$ of the system[4], k is Boltzmann's constant, T is the absolute temperature of the thermal bath and C is a normalization factor. Note that here and in the following we denote by 'state' of a system the ensemble of variables $\mathbf{x}$ which completely define its configuration.

The other fundamental relation describing the fluctuations around an equilibrium state is the fluctuation–dissipation theorem (FDT), stating that there is a direct relation between the fluctuation properties of a thermodynamic system and its linear response properties. The FDT is derived from the assumption of microscopic reversibility, as the response of a system in thermodynamic equilibrium to a small external perturbation is assumed to be the same as its response to a spontaneous fluctuation.

Let us consider a system surrounded by a reservoir, with temperature T (and pressure P), and assume that its state can be described through a set of observables x_i. Denote by $\langle x_i\rangle_0$ the canonical average of x_i over all the configurations of the unperturbed system at equilibrium with the surroundings; assuming that the system has a state of stable equilibrium, we can assume, without loss of generality, that $\langle x_i\rangle_0 = 0$. Therefore, the fluctuations of the system can be described through the correlation matrix

$$\sigma_{ij}(t,s) = \langle x_i(t)x_j(s)\rangle_0. \tag{1}$$

[4] More precisely, $\phi(\mathbf{x})$ is the reversible work that has to be applied to the system to bring it from the equilibrium state to its current state $\mathbf{x}$.

If the system is near its state of stable thermodynamic equilibrium, its free energy can be written as $\Delta G_0 = \frac{1}{2} g_{ij} x_i x_j$, with $g_{ij} = g_{ji}$. Therefore, according to EPT, the correlation matrix becomes $\sigma_{ij} = kT g_{ij}^{-1}$.

Now, assume that at time $t = 0$ a constant perturbation F_j, with $\|F_j\| = \epsilon$, is applied to the system, driving the expectation value of the variable x_i from $\langle x_i \rangle_0 = 0$ to $\langle x_i \rangle_\epsilon$. Here, F_j is the generalized force coupled to x_j, i.e. $F_j = \partial G_0 / \partial x_j$, where G_0 is the free energy of the unperturbed system. Accordingly, the dissipating properties of the system can be described in terms of the susceptibility,

$$\chi_{ij} = \lim_{\epsilon \to 0} \frac{\langle x_i(t) \rangle_\epsilon}{F_j} = \left(\frac{\partial \langle x_i(t) \rangle_\epsilon}{\partial F_j} \right)_{\epsilon = 0}. \tag{2}$$

The integrated form of FDT states that [9]

$$\sigma_{ij}(t,t) = kT \chi_{ij}(t), \tag{3}$$

where k is the Boltzmann constant. If the system is near its state of stable thermodynamic equilibrium, we obtain $F_j = g_{jk} x_k$ and $\chi_{ij} = g_{ij}^{-1}$, showing that FDT is identically satisfied.

Now, when the system is subjected to both conservative and non-conservative forces, the picture above becomes murky, and it is not clear which concept, if any, will take the place of the Boltzmann distribution or the temperature. So, for example, consider the motion of colloidal particles which are in thermal equilibrium with the fluid in which they are suspended and at the same time interact hydrodynamically with each other. From numerical simulation, we know that quantities such as the particle pair probability function and mean square velocity fluctuations do tend to steady state values, therefore suggesting that some sort of a 'thermodynamic' description of such systems should occur. However, we have no idea about how such steady state quantities could be determined *a priori*, and what they depend on.

In recent theoretical [3, 4] and experimental [5, 6] articles, it has been shown that the fluctuation–dissipation theorem (FDT) is violated in many cases. In particular, when the system is not too far from a stationary state (not necessarily corresponding to a state of stable equilibrium), it might admit a non-equilibrium temperature [7]. Such temperature can be defined through the static or the dynamic form of FDT, although the former seems to be more robust [8]. In particular, when the applied force moves the system away from its state of stable thermodynamic equilibrium and confines it to a harmonic well, Mauri and Leporini [8] showed that FDT can be generalized, defining a time-dependent temperature tensor $T_{ik}(t)$ as follows:

$$\chi_{ij}^{-1}(t) \sigma_{jk}(t) = kT_{ik}(t). \tag{4}$$

At $t = 0$, the system is at equilibrium, so that $T_{ij}(t = 0) = T\delta_{ij}$. At long time, though, the system may tend to another stationary, non-equilibrium state, characterized by a non-isotropic temperature tensor. A similar non-equilibrium temperature was defined in previous works [10, 11].

In this paper, without trying to solve this fundamental problem in its entirety, we concentrate on a particular case, namely the motion of a single Brownian particle in a fluid flow, subjected to both conservative and non-conservative forces. Apart from its simplicity, the great advantage of this problem is that for linear forces it reduces to the Ornstein–Uhlenbeck problem [2], therefore providing a way to check the validity of our

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results. The novelty of the approach presented here is that we use the path integral formulation, thus providing an alternate point of view which might help to solve similar problems in the future.

2. Description of the model

Consider a Brownian particle diffusing with diffusion coefficient $D = kT$, where the drag coefficient has been assumed to be normalized. Assuming that the Brownian particle is subjected to a force $\mathbf{F}$, the probability density satisfies the Fokker–Planck equation,

$$\frac{\partial P}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{J} = \delta(\mathbf{x} - \mathbf{x}_0)\delta(t); \qquad \mathbf{J} = \mathbf{F}P - kT\boldsymbol{\nabla}P. \tag{5}$$

Here, the force $\mathbf{F}$ coincides with the particle mean forward velocity [12],

$$\mathbf{F} = \mathbf{V}^+ = \frac{D^+\mathbf{x}(t)}{Dt} = \lim_{\Delta t \to 0} \frac{\langle \mathbf{x}(t + \Delta t) - \mathbf{x}(t)\rangle}{\Delta t}. \tag{6}$$

Now, let us assume that the system has a position of stable equilibrium, say $\mathbf{x} = \mathbf{0}$. Therefore, as $t \to \infty$, we expect a Boltzmann-like solution of this kind:

$$P(\mathbf{x}) = C \exp\left(-\frac{\psi(\mathbf{x})}{kT}\right), \tag{7}$$

where C is a normalization factor which can be determined from

$$\int P(\mathbf{x})\, \mathrm{d}\mathbf{x} = 1. \tag{8}$$

Substituting (7) into (5) we obtain

$$(\boldsymbol{\nabla}\psi) \cdot (\boldsymbol{\nabla}\psi + \mathbf{F}) = kT\boldsymbol{\nabla} \cdot (\boldsymbol{\nabla}\psi + \mathbf{F}). \tag{9}$$

Identical results could be obtained starting from the backward Fokker–Planck equation [12],

$$\frac{\partial P}{\partial t} + \boldsymbol{\nabla} \cdot (\mathbf{V}^- P + kT\boldsymbol{\nabla}P) = \delta(\mathbf{x} - \mathbf{x}_0)\delta(t), \tag{10}$$

which is expressed in terms of the particle mean backward velocity,

$$\mathbf{V}^- = \frac{D^-\mathbf{x}(t)}{Dt} = \lim_{\Delta t \to 0} \frac{\langle \mathbf{x}(t) - \mathbf{x}(t - \Delta t)\rangle}{\Delta t} = \mathbf{F} - 2kT\boldsymbol{\nabla}\log P = \mathbf{F} + 2\boldsymbol{\nabla}\psi. \tag{11}$$

Now, in general, the force $\mathbf{F}$ is the sum of a conservative and a non-conservative force, i.e. $\mathbf{F} = \mathbf{F}^{(\mathrm{c})} + \mathbf{F}^{(\mathrm{nc})}$, with $\boldsymbol{\nabla} \times \mathbf{F}^{(\mathrm{c})} = \mathbf{0}$ and $\boldsymbol{\nabla} \cdot \mathbf{F}^{(\mathrm{nc})} = 0$. Clearly, when the Brownian particle is subjected to a conservative force $\mathbf{F} = -\nabla\phi$, then the solution of equation (9) is simply $\psi = \phi$, so that the probability distribution (7) reduces to the Boltzmann distribution and EPT is satisfied. In addition, from its definition (2), we see that $\chi_{ij} = \partial^2\phi/\partial x_i \partial x_j = kT\sigma_{ij}^{-1}$, showing that in this case, as expected, FDT is identically satisfied as well.

Another interesting case arises when at any location the conservative and non-conservative forces are perpendicular to each other, i.e. $\mathbf{F}^{(\mathrm{c})} \cdot \mathbf{F}^{(\mathrm{nc})} = 0$. In fact, substituting $\psi = \phi$ into equation (9) we obtain $\mathbf{F}^{(\mathrm{c})} \cdot \mathbf{F}^{(\mathrm{nc})} = -kT\nabla \cdot \mathbf{F}^{(\mathrm{nc})} = 0$, so that we may conclude

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that in this case EPT is identically satisfied. However, unlike the case of conservative force fields, here FDT, in general, is not satisfied.

An alternative approach uses the Langevin equation,

$$\dot{\mathbf{x}} - \mathbf{F} = \mathbf{f}, \tag{12}$$

where $\dot{\mathbf{x}} = \mathbf{V}$ represents the particle mean velocity (otherwise [12] referred to as current velocity), while $\mathbf{f}$ is the Brownian force. Now, since $\mathbf{J} = P\dot{\mathbf{x}}$, from (5) we see that $\mathbf{f} = -kT\boldsymbol{\nabla}\log P$, so that

$$\mathbf{V} = \mathbf{F} + \boldsymbol{\nabla}\psi = \tfrac{1}{2}(\mathbf{V}^+ + \mathbf{V}^-). \tag{13}$$

In particular, in the case of conservative force fields, with $\mathbf{F} = -\boldsymbol{\nabla}\phi$ and $\psi = \phi$, we obtain $\mathbf{V}^+ = -\mathbf{V}^-$ and $\mathbf{V} = \mathbf{0}$.

3. Path integral approach

The path integral formulation of a diffusion process is due to Wiener [13] and has been since generalized by Feynman and Hibbs [14].

Considering that the Brownian force $\mathbf{f}$ in (12) results from the sum of a large number of collisions of the particle with the surrounding fluid, each occurring randomly and independently of the others, we have

$$\langle \mathbf{f}(t)\rangle = \mathbf{0}; \qquad \langle \mathbf{f}(t)\mathbf{f}(t+\tau)\rangle = 2kT\mathbf{I}\delta(\tau). \tag{14}$$

Applying the central limit theorem this result can be generalized, obtaining that the probability of observing a certain Brownian force function $\mathbf{f}(t)$ is the following Gaussian distribution:

$$P[\mathbf{f}(t)] \propto \exp\left[-\tfrac{1}{2}\int\int [\mathbf{f}(t)\mathbf{B}(\tau)\mathbf{f}(t+\tau)]\,\mathrm{d}t\,\mathrm{d}\tau\right], \tag{15}$$

where $\mathbf{B}$ is a sort of inverse of the variance of the process [15],

$$\mathbf{B}(\tau) = \langle \mathbf{f}(t)\mathbf{f}(t+\tau)\rangle^{-1} = \frac{1}{2kT}\mathbf{I}\delta(\tau). \tag{16}$$

Now, since $\mathbf{f}(t)$ and $\mathbf{x}(t)$ are linearly related through the Langevin equation, the probability $P[\mathbf{x}(t)]$ that the particle follows the path $\mathbf{x}(t)$ is proportional to $P[\mathbf{f}(t)]$. Consequently, substituting equations (12) and (16) into (15), we obtain [16]

$$P[\mathbf{x}(t)] = G(\mathbf{x},t)\exp\left[-\frac{1}{4kT}\int_{\mathbf{x}(t)} |\dot{\mathbf{x}} - \mathbf{F}|^2\,\mathrm{d}t\right]. \tag{17}$$

Here the normalizing term G is equal to the Jacobian,

$$G(\mathbf{x},t|\mathbf{x}_0) = \exp\left[-\int_0^t (\boldsymbol{\nabla}\cdot\mathbf{V})\,\mathrm{d}t\right], \tag{18}$$

where $\mathbf{V}$ is the current velocity (13). The Jacobian is the formal solution of the Fokker–Planck equation (5), i.e.,

$$P(\mathbf{x},t) = G(\mathbf{x},t|\mathbf{x}_0)\delta[\mathbf{x} - \mathbf{X}(t|\mathbf{x}_0)], \tag{19}$$

where $\mathbf{X}(t|\mathbf{x}_0)$ is the position of the particle at time t, assuming that at time $t = 0$ it was located at $\mathbf{x}_0$.

Finally, the conditional probability $P(\mathbf{x},t|\mathbf{x}_0)$ that the particle moves from $\mathbf{x}_0$ at time $t = 0$ to $\mathbf{x}$ at time t will be equal to the sum of the contributions (17) of all paths

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connecting the two points,

$$P(\mathbf{x}, t|\mathbf{x}_0) = \int P[\mathbf{x}(t)]\mathcal{D}[\mathbf{x}(t)], \tag{20}$$

where the integral is taken over all paths such that $\mathbf{x}(0) = \mathbf{x}_0$ and $\mathbf{x}(t) = \mathbf{x}$.

Substituting (17) into (20), we can write

$$P(\mathbf{x}, t|\mathbf{x}_0) = \int \exp\left[-\frac{S[\mathbf{x}(\tau)]}{4kT}\right]\mathcal{D}[\mathbf{x}(\tau)], \tag{21}$$

with

$$S[\mathbf{x}(t)] = \int_0^t L[\mathbf{x}(\tau), \tau]\,\mathrm{d}\tau, \tag{22}$$

and

$$L[\mathbf{x}(\tau), \tau] = |\dot{\mathbf{x}} - \mathbf{F}|^2 + 4kT\boldsymbol{\nabla}\cdot\mathbf{V}. \tag{23}$$

Here $S[\mathbf{x}(t)]$ is a sort of energy dissipated along the trajectory $\mathbf{x}(\tau)$ during the time interval t, while $L[\mathbf{x}(\tau), \tau]$ is the rate of energy dissipation at time τ. Note that, assuming that P is given by the Boltzmann-like distribution (7), from (13) we find $\boldsymbol{\nabla}\cdot\mathbf{V} = \boldsymbol{\nabla}\cdot(\mathbf{F}_c + \nabla\psi)$.

Among all paths, let us denote by $\mathbf{y}(\tau)$ the one that minimizes S. According to the Hamilton–Jacobi formalism of classical mechanics [17], the momentum $\mathbf{p}$ along the minimum path can be defined as

$$\mathbf{p} = \left[\frac{\partial L}{\partial \dot{\mathbf{x}}}\right]_{\mathbf{x}=\mathbf{y}} = 2(\dot{\mathbf{y}} - \mathbf{F}). \tag{24}$$

Now, defining the 'Hamiltonian' H (in reality, H has the units of an energy per unit time) as $H = \mathbf{p}\cdot\dot{\mathbf{y}} - L$, we obtain

$$H = \dot{y}^2 - F^2 - 4kT\,\boldsymbol{\nabla}\cdot\mathbf{V}. \tag{25}$$

The minimum path is determined explicitly through the Hamilton equation,

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{x}}, \tag{26}$$

that is

$$\dot{\mathbf{p}} + (\boldsymbol{\nabla}\mathbf{F})\cdot\mathbf{p} = 4kT\,\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{V}). \tag{27}$$

This equation could be obtained directly by applying the Euler–Lagrange equation to (23) and can be rewritten as

$$\ddot{\mathbf{y}} = \boldsymbol{\nabla}U + \dot{\mathbf{y}}\times\mathbf{B}, \tag{28}$$

where

$$U = \tfrac{1}{2}F^2 + 2kT\boldsymbol{\nabla}\cdot\mathbf{V}; \qquad \mathbf{B} = -\boldsymbol{\nabla}\times\mathbf{F}. \tag{29}$$

This equation generalizes the result obtained by Wiegler [18], who studied the motion of Brownian particles in conservative force fields. So, the minimum path describes the trajectory of a particle of unit mass and unit electric charge immersed in an electric field U and a magnetic field $\mathbf{B}$.

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It is intriguing that the dissipative motion of a Brownian particle is described in terms of the conservative motion of this 'particle', whose 'energy' H is constant. In fact, multiplying equation (28) by $\dot{\mathbf{y}}$ and considering that $\mathrm{d}/\mathrm{d}\tau = \dot{\mathbf{y}} \cdot \boldsymbol{\nabla}$, we can see that H is constant along the minimum path. Accordingly, since by definition

$$H = -\frac{\partial S_{\min}}{\partial t}, \tag{30}$$

we conclude that, at steady state, $H = 0$. Physically, the same conclusion could be reached observing that at the point of stable equilibrium, $\mathbf{x}_0 = \mathbf{0}$, we have $\mathbf{F} = \boldsymbol{\nabla}\psi = \mathbf{0}$.

Now, in general, the domain of integration of the path integral is composed of all paths whose distance from the minimum path is of order $\delta \sim kT/\tilde{F}$ or less, where $\tilde{F}$ is a typical value of $\mathbf{F}$. Therefore, expressing any path $\mathbf{x}(\tau)$ as the 'sum' of the minimum path $\mathbf{y}(\tau)$ and a 'fluctuating' part $\mathbf{x}'(\tau)$,

$$\mathbf{x}(\tau) = \mathbf{y}(\tau) + \mathbf{x}'(\tau), \tag{31}$$

where $\mathbf{x}'(0) = \mathbf{x}'(t) = 0$, then $S[\mathbf{x}(t)]$ can be expanded formally around $\mathbf{y}(\tau)$ as [15]

$$S[\mathbf{x}(t)] = S_{\min} + \frac{1}{2}\mathbf{x}' \cdot \left[\frac{\partial^2 S}{\partial \mathbf{x}' \partial \mathbf{x}'}\right]_{\mathbf{x}=\mathbf{y}} \cdot \mathbf{x}' + \cdots \tag{32}$$

with $S_{\min} = S[\mathbf{y}(t)]$, where we have considered that the first derivative is identically zero. From equations (22) and (23) we see that, if within distances of $\mathrm{O}(\delta)$ from the minimum path $\mathbf{F}$ can be approximated as a linear function, then S is a quadratic functional, and therefore the expansion (32) terminates after the second derivative, with the last term being a function of $\mathbf{x}'$ only, and not of $\mathbf{y}$ [19]. Finally, substituting (32) into (21)–(23) we obtain

$$P(\mathbf{x}, t|\mathbf{x}_0) = W(t) \exp\left[-\frac{1}{4kT}\int_0^t L_{\min}(\tau)\,\mathrm{d}\tau\right], \tag{33}$$

where $W(t)$ is a function of t only, and is independent of the endpoints, while $L_{\min}$ can be obtained from (23) and (25), considering that $H = 0$:

$$L_{\min}(\tau) = L[\mathbf{y}(\tau), \tau] = 2\dot{\mathbf{y}} \cdot (\dot{\mathbf{y}} - \mathbf{F}). \tag{34}$$

This result shows that under very general conditions the path integral is determined exclusively by the minimum path [18]. Clearly, equation (33) is the Boltzmann-like distribution (7), where

$$\psi = \tfrac{1}{4}S_{\min} = \tfrac{1}{4}\int_0^t L_{\min}(\tau)\,\mathrm{d}\tau. \tag{35}$$

Now, substituting (34) into (33) and considering that $\dot{\mathbf{y}}\mathrm{d}\tau = \mathrm{d}\mathbf{y}$, we see that equation (35) is identically satisfied, provided that

$$\dot{\mathbf{y}} = \mathbf{F} + 2\boldsymbol{\nabla}\psi = \mathbf{V}^-, \tag{36}$$

where $\mathbf{V}^-$ is the mean backward velocity (11). This equality shows that the velocity of the unit-mass particle along the minimum path coincides, locally, with the mean backward velocity of the Brownian particle. In particular, in the case of a conservative force field,

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$\mathbf{V}^- = -\mathbf{V}^+ = \boldsymbol{\nabla}\phi$, so that in (34) $L_{\min} = 4(\boldsymbol{\nabla}\phi)^2$, and therefore we obtain

$$P(\mathbf{x}, t|\mathbf{x}_0) = P(\mathbf{x}_0, t|\mathbf{x}). \tag{37}$$

This shows that the process is time reversible and therefore FDT is identically satisfied.

Finally, we may write the Hamilton–Jacobi equation substituting into (30) the expression (25) for H in which (cf equation (24)) $\mathbf{p} = \boldsymbol{\nabla}S_{\min} = 2(\dot{\mathbf{y}} - \mathbf{F})$, and $S_{\min} = 4\psi$, obtaining

$$(\boldsymbol{\nabla}\psi) \cdot (\boldsymbol{\nabla}\psi + \mathbf{F}) = kT\boldsymbol{\nabla} \cdot \mathbf{V} \tag{38}$$

where we have considered that the system is at steady state. From this equation, considering that $\mathbf{V} = \mathbf{F} + \boldsymbol{\nabla}\psi$, we easily obtain equation (9).

4. Linear case

A closed, analytical solution of these problems can be obtained in the linear case, describing a particle subjected to a linear attracting force, $F_i = -\Gamma_{ij}x_j$, which tends to restore the equilibrium state $\mathbf{x} = \mathbf{0}$. Consequently, the generalized susceptibility (2) is $\chi_{ij} = \Gamma_{ij}^{-1}$. Think, for example, of a particle immersed in a linear shear flow and attached to the origin with a spring, so that Γ_{ij} is the sum of a velocity gradient tensor $\Gamma_{ij}^{(1)}$, with $\Gamma_{ii}^{(1)} = 0$, and a spring constant $\Gamma_{ij}^{(2)} = K\delta_{ij}$. In this case, $F_i^{(\mathrm{c})} = -\Gamma_{ij}^{(s)}x_j$ and $F_i^{(\mathrm{nc})} = -\Gamma_{ik}^{(\mathrm{a})}x_k$, where $\Gamma_{ij}^{(\mathrm{s})}$ and $\Gamma_{ij}^{(\mathrm{a})}$ are the symmetric and antisymmetric parts of the $\boldsymbol{\Gamma}$ matrix. Naturally, if $\Gamma_{ij} = \Gamma_{ij}^{(\mathrm{s})}$, the applied force is conservative, i.e. $\mathbf{F} = -\nabla\phi$, with $\phi = \frac{1}{2}x_i\Gamma_{ij}^{(\mathrm{s})}x_j$ and, as we saw, both EPT and FDT are satisfied. Also, EPT is identically satisfied when the conservative force is perpendicular to the non-conservative force, that is when $\Gamma_{ij}^{(\mathrm{s})}\Gamma_{ik}^{(\mathrm{a})} = 0$. In general, as shown by Uhlenbeck and Ornstein [2], the solution of equation (9) is a Gaussian distribution, that is equation (7) with [20, 21]:

$$\psi = \frac{kT}{2}x_i\sigma_{ij}^{-1}x_j, \tag{39}$$

where σ_{ij} is the correlation tensor, $\sigma_{ij} = \langle x_ix_j\rangle$. Now, multiplying equation (12) by $\mathbf{x}$ and considering that $\langle f_ix_j\rangle = kT\delta_{ij}$, where the bracket denotes averaging, i.e. $\langle A(x)\rangle = \int A(x)P(x)\,\mathrm{d}x$, we see that at steady state we obtain

$$(\Gamma_{ik}\sigma_{kj})^{\mathrm{sym}} = kT\,\delta_{ij}, \tag{40}$$

showing that

$$\Gamma_{ik}\sigma_{kj} = kT_{ij} = k(T\delta_{ij} + T_{ij}^{(\mathrm{a})}), \tag{41}$$

where $T_{ij}^{(\mathrm{a})}$ is an antisymmetric tensor. The FDT (see equation (3) with $\chi_{ij} = \Gamma_{ij}^{-1}$) is valid only when this antisymmetric temperature tensor is identically zero. Obviously, this is also the solution of the Fokker–Planck equation[5].

Now, consider as an example of application the following 2D form of the $\boldsymbol{\Gamma}$ matrix:

$$\boldsymbol{\Gamma} = \begin{pmatrix} k_1 & -w_2 \\ w_1 & k_2 \end{pmatrix}, \tag{42}$$

[5] As shown in [20], the other condition, $kT\sigma_{ii}^{-1} = \Gamma_{ii}$, is identically satisfied by (40).

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where k_1 and k_2 are all positive, i.e. there must be a recovering force pushing the particle towards the origin.

Then, we find the following solution of equation (40):

$$\sigma_{ij} = \frac{kT}{(k_1+k_2)(k_1k_2+w_1w_2)} \begin{pmatrix} k_2(k_1+k_2)+w_2(w_1+w_2) & (k_1w_2-k_2w_1) \\ (k_1w_2-k_2w_1) & k_1(k_1+k_2)+w_1(w_1+w_2) \end{pmatrix}. \tag{43}$$

Consequently, since the the susceptibility χ_{ij} is defined such that $|x_i| = \chi_{ij}\, F_j$, in our case we obtain

$$\chi_{ij} = \Gamma_{ij}^{-1} = \frac{1}{(k_1k_2+w_1w_2)} \begin{pmatrix} k_2 & -w_1 \\ w_2 & k_1 \end{pmatrix}. \tag{44}$$

At this point, we can determine the tensorial non-equilibrium temperature (41), obtaining

$$T_{ij} = T \begin{pmatrix} 1 & -\frac{w_1+w_2}{k_1+k_2} \\ \frac{w_1+w_2}{k_1+k_2} & 1 \end{pmatrix} = T \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{w_1+w_2}{k_1+k_2} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}. \tag{45}$$

Therefore, we confirm that T_{ij} is the sum of a symmetric isotropic tensor $T^{(\mathrm{s})} = T\delta_{ij}$ and an antisymmetric tensor. The FDT is valid only when the antisymmetric temperature tensor is identically zero, which, in our case, requires that $w_1 = -w_2$. It is interesting to note that, taking the trace of equation (40), we obtain

$$kT = \frac{1}{d}\Gamma_{ij}\sigma_{ij}, \tag{46}$$

where d denotes the dimensionality of the problem.

Let us consider three particular cases.

- $w_1 = -w_2 = w$, i.e. Γ_{ij} is a symmetric tensor, corresponding to the case of a particle attached to the origin through a spring and immersed in an elongational flow. Then we find

$$\sigma_{12} = kT\frac{w}{w^2-k_1k_2}; \qquad \sigma_{11} = kT\frac{k_2}{k_1k_2-w^2}; \qquad \sigma_{22} = kT\frac{k_1}{k_1k_2-w^2} \tag{47}$$

  showing that indeed $\sigma_{ij} = kT\Gamma_{ij}^{-1}$. Therefore, since $T_{12} = 0$, we may conclude that, as expected, both FDT and EPT are satisfied.
- $w_1 = w_2 = w$, corresponding to the case of a particle attached to the origin through a spring and immersed in a rotational flow. Then, if the spring recovering force is isotropic, i.e. $k_1 = k_2 = A$, we find $\sigma_{12} = 0$ and $\sigma_{11} = \sigma_{22} = \sigma_{33} = kT/A$, showing that EPT is satisfied. On the other hand, $T_{12} = -Tw/A$, showing that FDT is violated. The fact that the equipartition theorem is satisfied is not surprising, as in this case $\Gamma_{ij}^{(\mathrm{s})}\Gamma_{ik}^{(\mathrm{a})} = 0$, i.e. conservative and non-conservative forces are perpendicular to each other.
- $w_1 = 0$ and $w_2 = -w$, which corresponds to a particle attached to the origin though a spring and immersed in a simple shear flow along the x_1-direction. Again, for an isotropic spring, with $k_1 = k_2 = A$, we obtain

$$\sigma_{12} = -\frac{kTw}{2A^2}; \qquad \sigma_{11} = kT\frac{2A^2+w^2}{2A^3}; \qquad \sigma_{22} = \frac{kT}{A}. \tag{48}$$

  Therefore, since $T_{12} = Tw/2A$, neither FDT nor EPT are satisfied.

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Equation (5) or (12) can also be solved in time, obtaining again a Gaussian distribution (7) and (39), where, in particular, $\sigma_{ij}(t)$ is the solution of the following equation.

$$\frac{\zeta}{2}\frac{\mathrm{d}\sigma_{ij}}{\mathrm{d}t} + (\Gamma_{ik}\sigma_{kj})^{\mathrm{sym}} = kT\delta_{ij}. \tag{49}$$

In particular, when $\omega_1 = \omega_2 = \omega$ and $k_1 = k_2 = A$, we obtain

$$\sigma_{ij}(t) = \sigma_{ij}^{(\mathrm{s})} + \Delta\sigma_{ij}\exp\left(-\frac{2At}{\zeta}\right), \tag{50}$$

where $\sigma_{ij}^{(\mathrm{s})}$ represents the steady state mean square displacement, while

$$\Delta\sigma_{11} = \sigma_{11}^{(0)} - \frac{\omega}{A}\sigma_{12}^{(0)} \tag{51}$$

$$\Delta\sigma_{22} = \sigma_{22}^{(0)} + \frac{\omega}{A}\sigma_{12}^{(0)} \tag{52}$$

$$\Delta\sigma_{12} = \sigma_{12}^{(0)} + \frac{\omega}{2A}(\sigma_{11}^{(0)} - \sigma_{22}^{(0)}) \tag{53}$$

is the unsteady part of the solution, with $\sigma_{ij}^{(0)} = \sigma_{ij}(t=0) - \sigma_{ij}^{(\mathrm{s})}$.

A shown in a recent article [8], although a time-dependent effective temperature can be defined by solving this problem, it turns out to be not very robust, so that it is preferable to describe the distance from equilibrium in terms of the stationary effective temperature (41).

Acknowledgment

Financial support from MIUR within the PRIN project 'Aging, fluctuation and response in out-of-equilibrium glassy systems' is gratefully acknowledged.

References

[1] Reif F, 1965 *Statistical Thermal Physics* (New York: McGraw-Hill)
[2] Uhlenbeck G E and Ornstein L S, *On the theory of the Brownian motion*, 1930 *Phys. Rev.* **36** 823
[3] Kurchan J, *In and out of equilibrium*, 2005 *Nature* **433** 223
[4] Crisanti A and Ritort F, *Violation of the fluctuation–dissipation theorem in glassy systems: basic notion and the numerical evidencs*, 2003 *J. Phys. A: Math. Gen.* **36** R181
[5] Berthier L and Barrat J-L, *Nonequilibrium dynamics and fluctuation–dissipation relation in a sheared fluid*, 2002 *J. Chem. Phys.* **116** 6228
[6] Carberry D M, Reid J C, Wang G M, Sevick E M, Searles D J and Evans D J, *Fluctuations and irreversibility: an experimental demonstration of a second-law-like thoerem using a colloidal particle held in an optical trap*, 2004 *Phys. Rev. Lett.* **92** 140601
[7] Evans D J and Searles D J, *The fluctuation theorem*, 2002 *Adv. Phys.* **51** 1529
[8] Mauri R and Leporini D, *Violation of the fluctuation–dissipation theorem in confined driven colloids*, 2006 *Europhys. Lett.* **76** 1022
[9] DeGroot S R and Mazur P, 1984 *Non-Equilibrium Thermodynamics* (New York: Dover)
[10] Cugliandolo L F, Kurchan J and Peliti L, *Energy flow, partial equilibration, and effective temperatures in systems with slow dynamics*, 1997 *Phys. Rev.* E **55** 3898
[11] Casas-Vazquez J and Jou D, *Temperature in non-equilibrium states: a review of open problems and current proposals*, 2003 *Rep. Prog. Phys.* **66** 1937
[12] Nelson E, 1985 *Quantun Fluctuations* (Princeton, NJ: Princeton University Press)
[13] Wiener N, *Generalized harmonic analysis*, 1930 *Acta Math.* **55** 117

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[14] Feynman R P and Hibbs A R, 1965 *Quantum Mechanics and Path Integrals* (New York: McGraw-Hill)
[15] Feynman R P, 1972 *Statistical Mechanics* (New York: Benjamin)
[16] Mauri R and Haber S, *Applications of the Wiener path integral for the diffusion of Brownian particles in shear flows*, 1986 *SIAM J. Appl. Math.* **46** 49
[17] Landau L D and Lifshitz E M, 1964 *Field Theory* (New York: Pergamon)
[18] Wiegler F W, 1986 *Introduction to Path Integral Methods in Physics and Polymer Science* (Singapore: World Scientific)
[19] Schulman L S, 1981 *Techniques and Applications of Path Integration* (New York: Interscience)
[20] Risken H, 1984 *The Fokker–Planck Equation* (Berlin: Springer)
[21] Gardiner C W, 1985 *Handbook of Stochastic Methods* (Berlin: Springer)