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A uniqueness-theorem for "linear" thermal baths

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Abstract

We consider systems in contact with a "linear" thermal bath, modeled by an additive thermal noise and an additive dissipation term which depends linearly on the system velocity. It is shown that the dissipation term and the bath temperature uniquely fix all statistical properties of the noise, without referring to any microscopic details of the bath. While the fluctuation dissipation theorem fixes only the second moment (correlation) of the noise, our present theorem extends to all moments. As a consequence, any linear thermal bath can be imitated by a harmonic oscillator bath model and the noise statistics is always Gaussian. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The canonical set up in equilibrium statistical mechanics is a system in contact with some thermal bath but otherwise isolated. Typical non-equilibrium problems arise if the system is in addition subjected to an external driving force, or if it is in contact with several thermal baths at different temperatures, or if one is interested in the relaxation towards equilibrium out of some far from equilibrium initial condition. [1] In all these cases, the very general and powerful principles of equilibrium statistical mechanics are no longer applicable, and in the absence of comparable non-equilibrium principles, a detailed modeling of the specific system dynamics under consideration and of the bath effects is unavoidable.

As demonstrated e.g. in Ref. [1], the effects of a thermal bath can always be divided into a systematic (deterministic) part (heat/energy dissipation *into* the bath) and a random (stochastic) part (fluctuating forces/noise *out of* the bath). The most widely used modeling of these two bath effects is based on the following *linearity* assumption (for a more precise formulation see Section 2): The "bare" dynamics of the isolated system is supplemented by an *additive* stochastic term ("fluctuating force") and an *additive* dissipative term ("frictional force"), which is furthermore assumed to be a *linear* functional of the system velocity only. Each bath contributes such a pair of terms and in the case of several baths they are simply *added* up. Examples are the standard models for the Brownian motion of a small particle (but "large" on a molecular scale) in a fluid [2], chemical reactions [3], Josephson junctions [4–6], and many others [7–9].

In some of these examples, the description of the bath effects is phenomenological, in others an approximative derivation from a reasonably realistic microscopic model is possible. In either case,

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[1] A further option, which we do not consider in this paper, consists in a non-thermal bath.

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from a fundamental viewpoint one may have concerns about whether such an approach may not bring along some subtle inconsistencies with basic principles of thermodynamics (e.g. contradictions to the second law [10–14]) and quantum mechanics (e.g. negative probabilities [15–20]).

Much like in mathematics [21], the only clean way to ensure that a phenomenological or approximative description is "well defined" in the above sense is by proving its "existence", that is, by deriving it from *some* microscopic model without any further approximations. Such an *existence-proof* for *any* "linear" thermal bath model with a *Gaussian* noise statistics is provided by the exactly solvable harmonic oscillator bath model, as developed originally in Refs. [22–24] and subsequently re-invented, refined, and generalized e.g. in Refs. [25–36,7–9].

The obvious next questions are: how *realistic* is the harmonic oscillator bath model, e.g. for a Brownian particle in a fluid or a chemical reaction in solution and what about "linear" thermal bath models with a *non-Gaussian* noise statistics? The answers readily follow from the main point of our present paper, namely the following *uniqueness-theorem*, as proven in Section 3: *for any "linear" thermal bath, the form of the dissipation term uniquely fixes all statistical properties of the fluctuating force term*. It should be emphasized that the well-known fluctuation dissipation theorem (of the second kind) [1,2,22,37–39] only fixes the correlation of the fluctuating force but does not say anything about its higher moments. In contrast, our theorem establishes the uniqueness of *all* moments and thus of all statistical properties of the fluctuations.

As a consequence, any "linear" thermal bath can be represented by a harmonic oscillator model, and in particular, the fluctuations are bound to satisfy a Gaussian statistics. This does not mean that the actual bath is a harmonic oscillator bath, but only that one cannot tell the difference as far as the effects on the system of interest are concerned [33]. Since an (approximately) "linear" character of the thermal bath is often very suggestive on the basis of theoretical arguments as well as experimental measurements, the harmonic oscillator model provides a rather satisfactory description of a thermal bath in a large variety of real situations [7–9,26,32–35,40], even though for many complex systems, one does not have a very clear understanding of the actual microscopic origin of the damping and fluctuation effects. In order to uniquely fix the thermal bath model, a decent approximation for the dissipation term is then sufficient, which may often be available from measurements or some theoretical considerations. On the other hand, the detailed statistical properties of the fluctuations, which might not have been so easily accessible a priori, are in fact no longer needed due to our present result.

2. Model

In order not to further obscure the already quite involved main ideas, we restrict ourselves to one-dimensional classical systems. The extension to higher dimensions is straightforward, while a quantum mechanical transcription brings along considerable additional complications. Our starting point is the simplest and most common model of a dissipative dynamics for a one-dimensional classical state variable $x(t)$, namely

$$m\ddot{x}(t) = F(x(t),t) - \int \eta(t-t')\dot{x}(t')\mathrm{d}t' + \xi(t), \qquad (1)$$

where dots indicate time derivatives and integration limits $\pm\infty$ are omitted. The first term on the right-hand side accounts for the deterministic, conservative system dynamics in the absence of any heat bath. It may, however, include some external driving forces, and especially in a higher dimensional generalization, may depend also on the system velocity $\dot{x}(t)$, e.g. for a charged particle in a magnetic field. The two other forces on the right-hand side of Eq. (1) model the effects of a thermal bath: The second term represents a systematic (deterministic) frictional force and the last term a stochastic fluctuating force (noise). Note that these two terms are not independent of each other since they both have the same origin, namely the interaction of the system $x(t)$ with a huge number of microscopic degrees of freedom of the thermal bath and that their random distribution according to some statistical mechanical ensemble gives rise to the stochastic nature of the fluctuating force $\xi(t)$. For reasons of causality, the damping kernel $\eta(t)$ has to respect the condition

$$\eta(t) = 0 \quad \text{for } t < 0. \tag{2}$$

Another restriction on $\eta(t)$ imposed by the second law of thermodynamics has been discussed in Ref. [33]. Apart from such basic constraints (see also Section 2.1 below), the damping kernel $\eta(t)$ in Eq. (1) may be arbitrary.

The state variable $x(t)$ in Eq. (1) may represent the position of a real Brownian particle [2], but also a chemical reaction coordinate [3], the phase difference of the macroscopic quantum mechanical wave function in a Josephson junction [4–6], or some other relevant (slow) collective coordinate of the system under study [7–9], with a correspondingly adapted meaning of the "mass" m and the various "forces" on the right-hand side of Eq. (1). By choosing $\eta(t)$ proportional to a delta function $\delta(t)$, Einstein's original model of Brownian motion with a memoryless damping is recovered [2], while in other contexts also a non-trivial memory of the damping may be physically relevant [7–9].

2.1. Linear thermal baths

Our goal in Section 3 will be to prove a general property for systems of the form (1). Since we will not refer to any microscopic details of the thermal bath, we have instead to provide a certain "minimal" set of "macroscopic" assumptions about how any decent thermal bath is supposed to behave. For instance, it can be shown [31,33] that a "bath" which consists of a single harmonic oscillator may already give rise to a dynamics of the general form (1) but can obviously not be considered as an admissible model for a real thermal bath as we have it in mind e.g. when stating the impossibility of a perpetuum mobile of the second kind.

We now collect all the assumption regarding the dynamics (1) and the associated thermal bath under which the uniqueness theorem from Section 3 is valid.

(i) We implicitly assume in Eq. (1) a kind of *linearity* of the bath effects in that the "bare" dynamics of the isolated system is supplemented by an *additive* dissipative term and an *additive* stochastic term. The dissipation is furthermore assumed to be a *linear* functional of the system velocity [2] and – as discussed below Eq. (2) – to respect causality and the second law of thermodynamics. Finally, if the system is simultaneously brought into contact with several thermal baths then each of them contributes one dissipation and one stochastic term, and all these terms can simply be *added* up on the right hand side of Eq. (1).

(ii) Our second assumption is a kind of *separability* of the thermal bath effects in the sense that changes of the system dynamics [3] do not change any properties of the thermal bath, i.e. of the last two terms in Eq. (1). First of all, this regards any changes of the mass m and the force field $F(x,t)$ in Eq. (1). Furthermore, this means that if the system is simultaneously in contact with several thermal baths then each of them acts exactly as if the others were not present. In this case, "separability" includes the additional assumption that each bath is isolated from all the others and that this reflects itself in the statistical independence of the respective noise terms. Finally, the state variable $x(t) =: x_1(t)$ can interact with additional macroscopic degrees of freedom $x_2(t), \ldots, x_N(t)$ without changing the properties of the last two term in Eq. (1) either. For example, in Fig. 1 the system is simultaneously interacting with two different baths and with a set of additional degrees of freedom. Though in practice this may be not easy to realize, in principle nothing speaks against the possibility that any of these interactions can be "switched off" without affecting the others in any way.

(iii) Our third assumption is the *thermality* of the bath effects, i.e. the word "thermal bath" is understood in the sense of equilibrium statistical mechanics. In detail this includes the following assumptions: (a): It is possible to associate a thermodynamical *temperature* T to each thermal

[2] Note that the integral in Eq. (1) can represent an arbitrary linear functional of the velocity if we understand $\eta(t)$ in the sense of distributions.

[3] Also the implicit assumption in Eq. (1) that the bath effects depend on the state of the system exclusively via the linear velocity dependence of the damping may be considered as part of the "separability" assumption.

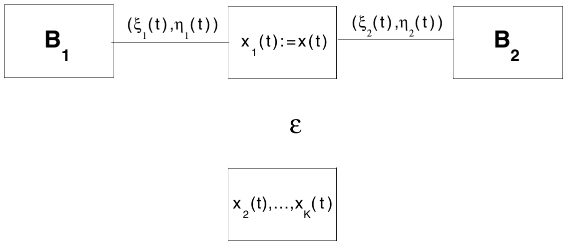

Fig. 1. The system of interest $x_1(t) := x(t)$, interacting simultaneously with two thermal baths B_1 and B_2, and in addition with the auxiliary degrees of freedom $x_2(t), \ldots, x_N(t)$. The interactions are symbolically indicated as $(\xi_1(t), \eta_1(t))$, $(\xi_2(t), \eta_2(t))$, and ϵ. Note that the bath B_2 is not related in any special way to the coordinate $x_2(t)$. Rather, both baths B_1 and B_2 interact solely with $x_1(t)$.

bath such that a system which permanently extracts energy out of one or several baths at the same temperature cannot exist. (b): The stochastic process $\xi(t)$ is *stationary*, that is, all statistical properties of $\xi(t + \Delta t)$ are identical to those of $\xi(t)$ for any time shift Δt. On condition that no time dependent external driving forces are acting and that the system cannot diverge to infinity, it is furthermore assumed that a stationary long time limit is reached, i.e., all expectation values approach a constant value. (c): The bath satisfies a *mixing* condition: For large time differences $t_2 - t_1 \to \infty$ the fluctuating forces $\xi(t_2)$ and $\xi(t_1)$ become statistically independent of each other, especially all correlations decay to zero. According to the fluctuation dissipation theorem [1,38,39], the latter property is equivalent to the condition $\eta(t) \to 0$ for $t \to \infty$.

We remark that as a consequence of (a) and (b) it follows that

$$\langle \xi(t) \rangle = 0, \tag{3}$$

where $\langle \cdot \rangle$ indicated an ensemble average over independent realizations of the stochastic process $\xi(t)$ in Eq. (1). Indeed, if Eq. (3) were not true for one t then stationarity would imply the same for all t and one could readily construct a perpetuum mobile of the second kind along the lines of (a). We further note that the mixing property (c) in combination with Poincaré's recurrence theorem excludes any heat bath with a finite number of microscopic degrees of freedom. The same can be inferred from the stationarity condition (b). In turn, only an infinite number of degrees of freedom guarantees an infinite heat capacity, as we expect it from any decent heat reservoir in the thermodynamic sense.

We close with a remark regarding the initial conditions in Eq. (1): For the sake of convenience, we implicitly assume that the system is permanently in contact with the bath(s) ever since the "initial time" $t = -\infty$. Due to the stationarity and mixing assumptions above, transients which depend on the corresponding initial conditions have therefore died out at any finite t. However, we can still "prepare" the system at our will by means of the force field $F(x, t)$, e.g. by forcing $x(t)$ into an extremely close vicinity of an arbitrary point x_0 during the time $t < t_0$, and then switching over to the actual force field of interest for $t > t_0$.

3. Uniqueness of the noise

In this section we consider a system (1) in contact with a thermal bath as specified in Section 2.1. We wish to prove that for any dissipation kernel $\eta(t)$ and any temperature T of the bath, all statistical properties of the noise $\xi(t)$ are uniquely fixed, independently of any microscopic details of the thermal bath.

To this end, we assume that there exists at least one further thermal bath with which the system (1) can interact and which exhibits the same damping kernel and the same temperature as the original thermal bath (otherwise there is no need for proving uniqueness). Labeling the two bath by "1" and "2" we thus have that

$$\eta_1(t) = \eta_2(t), \tag{4}$$

$$T_1 = T_2. \tag{5}$$

As discussed in item (ii) of Section 2.1, we can also couple both baths simultaneously to the system, and in doing so, the corresponding two fluctuating forces $\xi_1(t)$ and $\xi_2(t)$ are statistically independent.

Next we introduce the difference of the nth moments of these fluctuations:

$$D_n(t_1,\ldots,t_n) := \langle \xi_1(t_1)\cdots\xi_1(t_n)\rangle - \langle \xi_2(t_1)\cdots\xi_2(t_n)\rangle. \tag{6}$$

Since the statistical properties of the fluctuations are completely fixed by all its moments, it will be sufficient to proof that

$$D_n(t_1,\ldots,t_n) = 0 \quad \text{for all } t_1,\ldots,t_n \text{ and } n = 1,2,\ldots \tag{7}$$

To do so, we will proceed by induction: For $n = 1$, the property (7) holds true because of Eq. (3). In the rest of this section we consider an arbitrary but fixed $N \geqslant 2$ and take (7) for granted for any $n < N$. The aim is then to verify Eq. (7) for $n = N$.

For later convenience, we first rename the state variable $x(t)$ in Eq. (1) as

$$x_1(t) := x(t) \tag{8}$$

and similarly $m_1 := m$, $F_1(x,t) := F(x,t)$. Next, we supplement the system by $K-1$ additional degrees of freedom $x_2(t),\ldots,x_K(t)$, which all interact with $x_1(t)$ and with each other, but which have no direct contact with the two baths, cf. Fig. 1 and item (ii) in Section 2.1.

At this point we should emphasize once more the crucial role of the "separability" property (ii) from Section 2.1, saying that we can freely change the system dynamics without changing the bath properties. For this reason, it will be sufficient to proof (7) for one particular system, and we can in fact even choose a different system for every integer n and every time n-tuple in Eq. (7). In turn, once this uniqueness of the noise will have been proven in whatever way, it immediately carries over to any other system that possibly can be coupled to this bath. We have already exploited this freedom by coupling simultaneously another bath and the auxiliary state variables $x_2(t),\ldots,x_K(t)$ to the original system. In the following we will further exploit this freedom by choosing the dynamics of all the x_ks and especially their interaction according to our needs. Similarly, for the moment the integer K is still arbitrary. Later we will set $K = N$ if $N > 2$, whereas for $N = 2$ we will not need any of these additional degrees of freedom, i.e. formally we can set $K = 1$. The case $K = 2$ will always be tacitly excluded, and similarly for $K < 1$.

The dynamics of the K degrees of freedom $x_1(t),\ldots,x_K(t)$ is chosen as follows:

$$\hat{L}_k x_k(t) = \delta_{k,1}\xi(t) - \frac{\partial}{\partial x_k} V(x_1(t),\ldots,x_K(t)) \tag{9}$$

for $k = 1,\ldots,K$. Here $\delta_{k,1}$ is the Kronecker-delta and $\hat{L}_k$ is a linear operator, defined as

$$\hat{L}_k x_k(t) := m_k \ddot{x}_k(t) + \alpha_k x_k(t) + \delta_{k,1}\int \eta(t-s)\dot{x}_k(s)\mathrm{d}s, \tag{10}$$

where $m_k > 0$ and $\alpha_k > 0$ are model parameters that we can still freely choose according to our needs. Finally, $V(x_1,\ldots,x_K)$ is an interaction potential of the form

$$V(x_1,\ldots,x_K) := -\frac{\epsilon}{2}\sum_{k\neq j}^{K} x_j x_k - \epsilon^2 \prod_{k=1}^{K} x_k, \tag{11}$$

where ϵ is a small parameter, and where we have for the sake of simplicity assumed dimensionless units. The sum involves a shorthand notation for indicating that both k and j run from 1 to K with the exclusion of $k = j$.

According to Eq. (10), the left-hand side of (9) represents a deterministic, harmonic oscillator dynamics with frequency $\sqrt{\alpha_k/m_k}$ which is damped for $k = 1$ and undamped for $2 \leqslant k \leqslant K$. The right-hand side of (9) accounts for the noise, acting on the variable $x_1(t)$, and for the (anharmonic) coupling among the K harmonic oscillators. Since each of the two baths is contributing a dissipation and a noise term, we have according to the linearity assumption (i) from Section 2.1 that

$$\eta(t) = \eta_1(t) + \eta_2(t), \tag{12}$$

$$\xi(t) = \xi_1(t) + \xi_2(t). \tag{13}$$

Note that our intention to prove some very general statement about arbitrary thermal baths without any reference to the microscopic details is very similar in spirit to the typical situations encountered in equilibrium thermodynamics. Accordingly, much like for the invention of problem adapted thermodynamic "cycle processes", the above specific choice of the harmonic oscillator dynamics and especially of the anharmonic interaction is largely a matter of intuition and trial and error. The ultimate justification for this choice is that it will do what we want it to do. It is likely that there exists other choices which would work as well, possibly even simpler ones. The physical picture by which we were guided was the following: If the two noises $\xi_1(t)$ and $\xi_2(t)$ were not statistically identical then it should be possible to "filter" certain frequency type features out of these noises and to exploit them for constructing a perpetuum mobile of the second kind. As it turns out, for exploiting in this way dissimilarities in the second moments ($N = 2$) of $\xi_1(t)$ and $\xi_2(t)$, a single harmonic oscillator suffices ($K = 1$ and/or $\epsilon = 0$), while for higher moments ($N > 2$) more and more interacting, non-linear oscillators are needed ($K = N$ and $\epsilon > 0$).

We further remark that the total potential of the K-dimensional dynamics (9), given by the individual harmonic oscillator potentials plus the interaction potential (11), does not diverges towards $+\infty$ in all directions of the K-dimensional configuration space, but rather to $-\infty$ in certain directions for any [4] $\epsilon \neq 0$. However, for very small ϵ the total potential is practically harmonically increasing in all directions for not too large x_k-values. With decreasing ϵ, the system has to overcome higher and higher potential barriers before reaching the asymptotically decreasing regions of the total potential. Since the noise induced crossings of such barriers becomes extremely unlikely as ϵ decreases, they can be neglected. Alternatively, one may introduce "saturation terms" into the total potential which guarantee a divergence towards $+\infty$ in all directions, but which would only have any notable effect in regions which are practically never visited anyway. We thus can assume that the preconditions for items (iiia) and (iiib) in Section 2.1 are guaranteed. The latter item (iiib) implies stationarity of expectation values, in particular

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle[\xi_1(t) - \xi_2(t)]x_1(t)\rangle = 0. \tag{14}$$

Finally, we note that the total force $F_i(t)$ exerted on the system $x_1(t)$ by the ith bath ($i = 1, 2$) is given by

$$F_i(t) := -\int \eta_i(t-s)\dot{x}_1(s)\mathrm{d}s + \xi_i(t) \tag{15}$$

see Eqs. (1), (8), (12) and (13). The corresponding power $F_i(t)\dot{x}_1(t)$ has to vanish on the average, otherwise a permanent energy transfer from one into the other bath would result. Since we are dealing with two thermal baths at the same temperature (5), this would contradict item (iiia) from Section 2.1. Invoking stationarity once again, we can conclude that

$$\begin{aligned} 0 &= \langle F_1(t)\dot{x}_1(t)\rangle - \langle F_2(t)\dot{x}_1(t)\rangle \\ &= \langle[\xi_1(t) - \xi_2(t)]\dot{x}_1(t)\rangle, \end{aligned} \tag{16}$$

where we have exploited (4) in the last identity. By taking advantage of Eq. (14), it finally follows that

$$\frac{\mathrm{d}}{\mathrm{d}s}\langle[\xi_1(s) - \xi_2(s)]x_1(t)\rangle|_{s=t} = 0. \tag{17}$$

Next we introduce Green's functions, uniquely defined by the requirements that

$$\hat{L}_k G_k(t) = \delta(t) \tag{18}$$

$$G_k(t < 0) = 0. \tag{19}$$

The unique solution of Eq. (9) respecting the "stationarity" condition (iiib) from Section 2.1 then reads

$$\begin{aligned} x_k(t) = \int \mathrm{d}t' G_k(t-t')\Bigg[&\delta_{k,1}\xi(t') + \epsilon\sum_{j\neq k}^{K} x_j(t') \\ &+ \epsilon^2 \prod_{j\neq k}^{K} x_j(t')\Bigg], \end{aligned} \tag{20}$$

see also the discussion of the initial conditions at the end of Section 2.1. By introducing Eq. (20) into itself, one finds for $K = 1, 3, 4, 5, \ldots$ (but not for $K = 2$) the result

[4] The situation is not improving by changing the signs on the right-hand side of Eq. (11).

$$x_1(t) = \int dt' \big[G_1(t-t') + \epsilon H_2(t-t') + \epsilon^3 H_3(t-t')\big]\xi(t') + \epsilon^3 \prod_{j\neq 1}^{K} \int dt' G_1(t-t') \int dt'' G_j(t'-t'') \times \int dt''' G_1(t''-t''')\xi(t''') + \mathcal{O}(\epsilon^4), \quad (21)$$

where we have defined

$$H_2(t) := \sum_{j\neq 1}^{K} \int dt_1 G_1(t-t_1) \int dt_2 G_j(t_1-t_2) G_1(t_2), \quad (22)$$

$$H_3(t) : = \sum_{j\neq 1}^{K} \sum_{k\notin\{1,j\}}^{K} \int dt_1 G_1(t-t_1) \times \int dt_2 G_j(t_1-t_2) \int dt_3 G_k(t_2-t_3) G_1(t_3). \quad (23)$$

Our next step is to introduce Eq. (21) into Eq. (17) and then equating terms of equal order in ϵ. Observing Eq. (13) we obtain in order ϵ^0 the result

$$\frac{d}{ds}\left\langle [\xi_1(s) - \xi_2(s)] \int dt' G_1(t-t')\big[\xi_1(t') + \xi_2(t')\big]\right\rangle\bigg|_{s=t} = 0. \quad (24)$$

Recalling that $\xi_1(t)$ and $\xi_2(t)$ are statistically independent and exploiting Eqs. (3) and (6) we can infer that

$$\int dt' G_1(t-t') \frac{\partial}{\partial t} D_2(t,t') = 0. \quad (25)$$

According to item (iiia) in Section 2.1 the thermal noises $\xi_1(t)$ and $\xi_2(t)$ are stationary, implying that $D_2(t,t') = D_2(t-t',0)$. From the definition (6), the property $D_2(-t,0) = D_2(t,0)$ is obvious, while the mixing property (iiic) from Section 2.1 implies that $D_2(t,0) \to 0$ for $t \to \infty$. To verify Eq. (7) for $n = 2$ it is therefore sufficient to demonstrate that the relation

$$\int dt G_1(t) \frac{\partial}{\partial t} D_2(t,0) = 0 \quad (26)$$

implies $(\partial/\partial t)\ D_2(t,0) = 0$ for all $t \geqslant 0$.

At this point one has to exploit the fact that the parameters m_1 and α_1 in (10) are still at our disposition, and hence Eq. (26) has to be valid for *any* m_1, $\alpha_1 > 0$. According to Eqs. (18) and (19), the left-hand side of Eq. (26) may be looked upon as the position $x_1(t)$ at time $t = 0$ of a damped deterministic oscillator that has been subject to the driving force $(\partial/\partial t)\ D_2(-t,0)$ during the time $t \leqslant 0$. Physically, it is quite plausible that this position $x_1(0)$ can only be zero for all choices m_1, $\alpha_1 > 0$ if this driving force $(\partial/\partial t)\ D_2(-t,0)$ identically vanishes for all $t \leqslant 0$.

Mathematically, the same follows if we can show that $G_1(t)$ is a complete function system with respect to its parameters m_1, $\alpha_1 > 0$ on the positive real axis $t \geqslant 0$. To this end, we perform a Fourier transformation in Eqs. (10) and (18) with the result

$$P_1(\omega)\widetilde{G}_1(\omega) = 1, \quad (27)$$

$$P_1(\omega) := -m_1\omega^2 + i\omega\tilde{\eta}(\omega) + \alpha_1, \quad (28)$$

where the Fourier transform $\tilde{f}(\omega)$ of a function $f(t)$ is defined as

$$\tilde{f}(\omega) := \int dt e^{-i\omega t} f(t). \quad (29)$$

The general solution of Eq. (27) can be written as

$$\widetilde{G}_1(\omega) = \frac{1}{P_1(\omega)} + \sum_{P(\omega_i)=0} C_i \delta(\omega - \omega_i) \quad (30)$$

with free integration constants C_i. From the condition (19) one can infer that all these constants must be zero. The remaining Fourier back-transformation is possible in analytical form only for large values of m_1 and α_1. In this case, the zeros of $P_1(\omega)$ can be approximately determined and the method of residues yields the asymptotically exact approximation

$$G_1(t) = \mathcal{N}_1 \Theta(t) \sin(\omega_1 t) e^{-\lambda_1 t}, \quad (31)$$

where $\Theta(t)$ is the Heaviside step function and where

$$\omega_1 = \omega_1(m_1,\alpha_1) := \sqrt{\frac{\alpha_1}{m_1}} + \frac{\mathrm{Im}[\tilde{\eta}(\sqrt{\alpha_1/m_1})]}{2m_1} + \mathcal{O}(m_1^{-2}), \quad (32)$$

$$\lambda_1 = \lambda_1(m_1, \alpha_1) := \frac{\mathrm{Re}[\tilde{\eta}(\sqrt{\alpha_1/m_1})]}{2m_1} + \mathcal{O}(m_1^{-2}), \tag{33}$$

$$\mathcal{N}_1 = \mathcal{N}_1(m_1, \alpha_1) := [m_1\omega_1(m_1, \alpha_1)]^{-1}. \tag{34}$$

We thus recover a for large m_1 and α_1 the physically expected weakly damped harmonic oscillations (31) with a frequency (32) close to the undamped frequency $\sqrt{\alpha_1/m_1}$, supplemented by a weak damping (33) that is governed by the Fourier transformed damping kernel at the unperturbed frequency $\sqrt{\alpha_1/m_1}$. Note that the mixing condition (iiic) from Section 2.1 guarantees that $\mathrm{Re}[\tilde{\eta}(\omega)] < \infty$ and that we also recover the condition $\mathrm{Re}[\tilde{\eta}(\omega)] \geqslant 0$ as a consequence of the second law of thermodynamics [33]. Finally, we go over from m_1 and α_1 to ω_1 and λ_1 as independent model parameters. While m_1 and α_1 were restricted to very large values, the corresponding values of ω_1 in Eq. (32) can still practically vary over the entire positive real axis, while λ_1 in Eq. (33) is now restricted to very small values. It thus follows with Eq. (26) that

$$\int_0^\infty \mathrm{d}\omega_1 g_1(\omega_1) \int \mathrm{d}t G_1(t) \frac{\partial}{\partial t} D_2(t, 0) = 0 \tag{35}$$

for arbitrary weight functions $g_1(\omega_1)$. Choosing

$$g_1(\omega_1) := (2/\pi\mathcal{N}_1)\sin(\omega_1 t_1)\mathrm{e}^{\lambda_1 t_1} \tag{36}$$

it follows with Eq. (31) for any $t_1 > 0$ that

$$\int_0^\infty \mathrm{d}\omega_1 g_1(\omega_1) G_1(t) = \delta(t - t_1). \tag{37}$$

In view of Eq. (35) we finally can conclude that indeed $(\partial/\partial t_1)\, D_2(t_1, 0) = 0$ for any $t_1 > 0$.

Next we turn to the proof of Eq. (7) for an arbitrary $n = N \geqslant 3$, assuming that the relation is valid for all $n < N$. Introducing Eq. (21) into Eq. (17) and observing Eq. (13), we see that the contribution from the first line on the right-hand side of Eq. (21) vanishes due to the validity of Eq. (7) for $n = 2$. Focusing on terms of order ϵ^3, i.e. the second line in Eq. (21), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}s}\left\langle [\xi_1(s) - \xi_2(s)] \prod_{j\neq 1}^{K} \int \mathrm{d}t' G_1(t - t')] \times \int \mathrm{d}t'' G_j(t' - t'') \int \mathrm{d}t''' G_1(t'' - t''') \times \left[\xi_1(t''') + \xi_2(t''')\right] \right\rangle\Bigg|_{s=t} = 0. \tag{38}$$

Similarly as in Eq. (31) one finds the following solution of Eqs. (18)–(20):

$$G_k(t) = \mathcal{N}_k \Theta(t)\sin(\omega_k t), \quad k = 2, \ldots, K, \tag{39}$$

$$\omega_k = \omega_k(m_k, \alpha_k) := \sqrt{\alpha_k/m_k}, \tag{40}$$

$$\mathcal{N}_k = \mathcal{N}_k(m_k, \alpha_k) := [m_k\omega_k(m_k, \alpha_k)]^{-1}, \tag{41}$$

which is exact for arbitrary $m_k, \alpha_k > 0$ in Eq. (10). Like in Eqs. (36) and (37) we now go over to ω_k in place of α_k as independent model parameter and we define

$$g_k(\omega_k) := (2/\pi\mathcal{N}_k)\sin(\omega_k t_k) \tag{42}$$

with the consequence that

$$\int_0^\infty \mathrm{d}\omega_k g_k(\omega_k) G_k(t) = \delta(t - t_k) \tag{43}$$

for any $t_k > 0$ and $k = 2, \ldots, K$. By operating from the left-hand side with factors of the form $\int_0^\infty \mathrm{d}\omega_k g_k(\omega_k)\cdots$ we can thus transduce each integrand G_k in Eq. (38) into a δ-function and then carry out the integrals. With the particular choice $K = N$ and $t_1 = 0$ one arrives in this way at the result

$$\frac{\mathrm{d}}{\mathrm{d}s}\left\langle [\xi_1(s) - \xi_2(s)] \prod_{j\neq 1}^{N} [\xi_1(t - t_j) + \xi_2(t - t_j)] \right\rangle\Bigg|_{s=t} = 0. \tag{44}$$

Recalling that the two noises $\xi_1(t)$ and $\xi_2(t)$ are statistically independent and by observing that for every summand arising in Eq. (44) there exists a summand with all the indices of the noises $\xi_1(t)$ and $\xi_2(t)$ exchanged and with inverted sign, one can infer that the resulting sum consists of one summand $(\partial/\partial t)\, D_N(t, t - t_2, \ldots, t - t_N)$, while all the remaining summands are proportional to terms D_n with $n < N$ and are therefore zero. In other words, we can conclude that

$$\frac{\partial}{\partial t} D_N(t, t - t_2, \ldots, t - t_N) = 0. \quad (45)$$

Here, $t_2, \ldots, t_N$ are still restricted to positive values, but due to the symmetry of the arguments in the definition (6) one readily sees that this is sufficient to conclude that

$$\frac{\partial}{\partial t} D_N(t_1, \ldots, t_N) = 0 \quad (46)$$

for arbitrary $t_1, \ldots, t_N$. Exploiting the mixing property (iiic) from Section 2.1 and the validity of Eq. (7) for $n < N$ one can infer that

$$\lim_{t_1 \to \infty} D_N(t_1, \ldots, t_N) = 0. \quad (47)$$

Combining this result with Eq. (46) finally implies that

$$D_N(t_1, \ldots, t_N) = 0 \quad (48)$$

for arbitrary $t_1, \ldots, t_N$. Hence our proof by induction of Eq. (7) is completed.

4. Concluding remarks

As the central result of our present paper we have shown that for any "linear" thermal bath, as specified in Section 2.1, the dissipation kernel and the temperature of the bath uniquely fix all statistical properties of the thermal noise, independent of any further details of the microscopic bath dynamics. In contrast to the mathematical details of the proof, the basic physical picture behind it is quite simple: If there were any arbitrariness in the statistical properties of the thermal noise then it should be possible to "filter" out these non-uniquely defined features in some way and exploit them for constructing a perpetuum mobile of the second kind. As usual in thermodynamics, figuring out an adequate "thermodynamic machine" which does the job (as "elegantly" as possible) requires some creativity and technical skills. As a reward one obtains very general conclusions without reference to any microscopic details. It was only after our proof has been completed that it came to our attention that an approach somewhat similar in spirit has in fact already been adopted by Nyquist in his celebrated 1928 paper [38], and also in Section III of [33]. Apart from this general spirit, both these works are, however, completely different from ours and also simpler in so far as only harmonic oscillator systems are involved, while our proof crucially depends on the presence of anharmonic terms.

Since the effects of any "linear" thermal can be reproduced by an appropriately chosen harmonic oscillator bath model, it follows that the thermal noise of any "linear" thermal bath satisfies a Gaussian statistics. On the other hand, various heuristic arguments of why the harmonic oscillator bath is such a versatile tool have been given in the past [26,32,33]. Especially, throughout the latter work [33], the Gaussianity of the fluctuations is taken for granted without any further discussion. Our uniqueness theorem is one important step forward to make these arguments rigorous.

Playing devil's advocate one might argue that the "linear" structure of the bath effects is already so restrictive that the harmonic oscillator model is probably the only microscopic dynamics which strictly reproduces this structure. While we know of several experts in the field to which such a statement has appeared quite plausible, any somewhat more tangible argument in favor of it seems to be absent. On the other hand, e.g. for a real Brownian particle in a fluid, a "linear" thermal bath model is clearly an excellent approximation while a harmonic oscillator model for the actual microscopic dynamics of the fluid is obviously very unrealistic. In this case the (at least in very good approximation) "linear" character of the bath seems not to be rooted in harmonically coupled harmonic oscillators but rather in a huge number of very weak and almost independent "random" impacts of the surrounding molecules.

Interesting open problems are the generalization of our approach for so-called multiplicative noise, the question of whether the noise statistics in turn uniquely fixes the dissipation term, and possible relaxations in the assumptions from Section 2.1 such as to include e.g. non-mixing baths or even baths consisting of a finite number of degrees of freedom.

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References

[1] H. Grabert, P. Hänggi, P. Talkner, J. Stat. Phys. 22 (1980) 537.
[2] A. Einstein, Ann. Phys. (Leipzig) 17 (1905) 549.
[3] H.A. Kramers, Physica (Utrecht) 7 (1940) 284.
[4] W.C. Steward, Appl. Phys. Lett. 12 (1968) 277.
[5] D.E. McCumber, J. Appl. Phys. 39 (1968) 3113.
[6] A. Barone, G. Paterno, Physics and Applications of the Josephson Effect, Wiley, New York, 1982.
[7] P. Hänggi, P. Talkner, M. Borkovec, Rev. Mod. Phys. 62 (1990) 251.
[8] R.F. O'Connell, Int. J. Quant. Chem. 58 (1996) 569.
[9] U. Weiss, Quantum Dissipative Systems, second enlarged edition, World Scientific, Singapore, 1999.
[10] L. Brillouin, Phys. Rev. 78 (1950) 627.
[11] R. McFee, Am. J. Phys. 39 (1971) 814.
[12] R.D. Astumian, P.B. Chock, T.Y. Tsong, Y. Chen, H.V. Westerhoff, Proc. Natl. Acad. Sci. USA 84 (1987) 434.
[13] V. Capek, T. Mancal, Europhys. Lett. 48 (1999) 365.
[14] N.G. van Kampen, Stochastic Processes in Physics and Chemistry, revised and enlarged edition, North-Holland, Amsterdam, 1992.
[15] R. Dümcke, H. Spohn, Z. Phys. B 34 (1979) 419.
[16] P. Talkner, Ann. Phys. (New York) 167 (1986) 390.
[17] V. Ambegaokar, Ber. Bunsenges. Phys. Chem. 95 (1991) 400.
[18] P. Pechukas, Phys. Rev. Lett. 73 (1994) 1060.
[19] G.W. Ford, R.F. O'Connell, Phys. Rev. Lett. 77 (1996) 798.
[20] S. Gnutzmann, F. Haake, Z. Phys. B 101 (1996) 263.
[21] P.J. Davis, R. Hersch, The Mathematical Experience, Birkhäuser, Boston MA, 1981.
[22] A. Einstein, L. Hopf, Ann. Phys. (Leipzig) 33 (1910) 1105.
[23] N.N. Bogolyubov, On some statistical methods in mathematical physics, Publ. Acad. Sci. Ukr. SSR, 1945, pp. 115–137 (in Russian).
[24] V.B. Magalinskii, Sov. Phys. JETP 9 (1959) 1381 [JETP 36 (1959) 1942].
[25] R.J. Rubin, J. Math. Phys. 1 (1960) 309.
[26] R.P. Feynman, F.L. Vernon, Ann. Phys. (New York) 24 (1963) 118.
[27] P. Ullersma, Physica (Utrecht) 32 (1966) 27.
[28] P. Ullersma, Physica (Utrecht) 32 (1966) 56.
[29] P. Ullersma, Physica (Utrecht) 32 (1966) 74.
[30] P. Ullersma, Physica (Utrecht) 32 (1966) 90.
[31] R. Zwanzig, J. Stat. Phys. 9 (1973) 215.
[32] A.O. Caldeira, A.J. Leggett, Ann. Phys. (New York) 149 (1983) 374 erratum: Ann. Phys. (New York) 153 (1984) 445.
[33] G.W. Ford, J.T. Lewis, R.F. O'Connell, Phys. Rev. A 37 (1988) 4419.
[34] H. Grabert, P. Schramm, G.-L. Ingold, Phys. Rep. 168 (1988) 115.
[35] V.A. Benderskii, D.E. Makarov, C.A. Wight, Adv. Chem. Phys. 88 (1994) 1.
[36] P. Hänggi, in: L. Schimansky-Geier, T. Pöschel (Eds.), Lecture Notes in Physics, vol. 484, Springer, Berlin, 1997.
[37] J.B. Johnson, Phys. Rev. 32 (1928) 97.
[38] H. Nyquist, Phys. Rev. 32 (1928) 110.
[39] H.B. Callen, T.A. Welton, Phys. Rev. 83 (1951) 34.
[40] G. Schön, A.D. Zaikin, Phys. Rep. 198 (1990) 237.