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Statistical Physics of Random Systems

Stochastic Theories of Randomly Modulated Systems

Ryogo KUBO
Department of Physics, University of Tokyo, Tokyo, Japan

Statistical mechanics aims at providing us with theoretical methods to treat physical systems consisting of a great number of degrees of freedom. We are usually concerned with a certain projection of the motion of the entire system; for example we observe a Brownian particle under a microscope. Such a projected motion will necessarily bear a stochastic nature, because a great part of the microscopic information is lost by projection. We may formulate the problem generally in the following way. We observe a physical system A which is in contact with a large bath B. The bath B exerts a force on A which may be regarded as stochastic and induces a stochastic motion of A. In a very wide meaning of the word, we may call this sort of stochastic motion as a Brownian motion. The purpose of the present paper is to give a few remarks on stochastic consideration of the Brownian motion.

Let us first recall the well-known Langevin equation of a classical Brownian particle.[1] The equation is written as

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\gamma p + R(t) \equiv F(t) \ , \tag{1}$$

where p is the momentum of the Brownian particle, γ is the friction constant and R is the random force. The sum, $F(t)$, of the friction force and the random force is the total force exerted on the particle by the medium (bath) surrounding the particle. More generally we may suppose a system A described by a set of dynamical variables a and assume the equation of motion to be written as

$$\frac{\mathrm{d}a}{\mathrm{d}t} = F(a, t) \ , \tag{2}$$

where $F(a, t)$ is a stochastic process. It may be non-linear in a and also may be non-local in time; namely, it may in general depend on the past history of the motion. Equation (1) or (2) describes the Brownian motion of the system A in its natural environment. When the system A is brought under a process of observation in which an external force K is exerted from an outside source and the response of A is observed, the stochastic equation is replaced by

$$\frac{\mathrm{d}a}{\mathrm{d}t} = F(a, t) + K(t) \ . \tag{3}$$

Equation (1) or (2) may be used for determination of the unperturbed Brownian motion of the system and eq. (3) for determination of the response of the system to K. These equations are defined by specifying the basic random process incorporated in the process R or F.

We may call this sort of approach a stochastic theory of a randomly modulated system. As a phenomenological theory, one will not necessarily be bothered how one derives the stochastic properties of R or F by the first principles from the known structure of the bath and the interaction. One may take a phenomenological viewpoint and introduce reasonable assumptions for the underlying stochastic process defining the stochastic equations. One may regard this as a retreat from the front of the modern statistical mechanics. However the value of a phenomenological approach should be appreciated sometimes particularly when our physical insight is blurred by technicals of the modern methods.

The basic problems in such a phenomenological approach will be the following:

(I) How do we incorporate the random interaction of the bath and the system into the dynamical equation of the system?

(II) How are the physical conditions of the bath represented in the stochastic character of the interaction?

(III) Given the basic stochastic process in the dynamics of the system, how do we determine the Brownian motion of the system and how do we predict the response of the system to an external observation?

These problems are of course mutually related. They are answered very clearly by eq. (1) for the classical example of the Brownian motion of a free particle. In this example, the friction force acts without retardation and correspondingly the random force has a white noise and furthermore it is a Gaussian process. These assumptions are adequate to describe a heavy Brownian particle floating in a liquid and can be proved from a microscopic ground for an idealized model. The friction constant γ is related to the random force by the equation

$$\gamma=\frac{1}{\langle p^2\rangle}\int_0^\infty \langle R(t+t_0)R(t_0)\rangle \mathrm{d}t\ , \tag{4}$$

which is an example of the fluctuation-dissipation theorem.[1,2] This relation and the Gaussian assumption assure the Maxwellian distribution for the momentum of the particle in equilibrium. This can be shown in many ways, for example, using the Rice method or the Fokker-Planck equation. This simplicity of the theory is mainly due to the fact that the random variable p in eq. (2) is linear in the random force.

We would of course like to generalize the theory in order to cover much wider categories. Generally speaking, the random force may not be Gaussian, its spectrum may not be white and the equation of motion may not be linear in the dynamical variables and in the random force. Such generalizations cannot easily be achieved and so the present status of the theory is rather unsatisfactory from a general point of view, although some remarkable progress has been made in recent years.[3]

We now would like to start from some simple cases where there are not much difficulties for the basic questions (I) and (II). They are the cases in which the reaction of the system A to the bath can safely be ignored. In such a case we are allowed to assume a random Hamiltonian $\mathscr{H}(t)$ defining the interaction of the system with the bath and write a Schödinger equation

$$\frac{\partial\psi}{\partial t}=\frac{1}{i\hbar}\mathscr{H}(t)\psi\ , \tag{5}$$

for the state vector ψ of A or an equation of motion

$$\frac{\partial\rho}{\partial t}=\frac{1}{i\hbar}[\mathscr{H}(t),\rho]\ , \tag{6}$$

for the density matrix ρ. We have here chosen a quantal expression for the sake of generality, specialization to classical cases being obvious.

The Hamiltonian $\mathscr{H}(t)$ is considered as random. More explicitly we assume that $\mathscr{H}$ is a function of a random variable $x(t)$ which is a c-number or a set of c-numbers. This means that the random variable $x(t)$ has no internal degrees of freedom so that the possibility is excluded to consider the reaction of the system to the dynamical motion of the bath. Further we assume that the process $x(t)$ is essentially Markoffian in the sense that it can be supplemented with additional variables to form a complete set of random variables λ which make a Markoffian process. Namely we assume that the equation

$$\frac{\partial}{\partial t}P(\lambda,t)=\Gamma_\lambda P(\lambda,t)\ , \tag{7}$$

holds for the probability $P(\lambda,t)$ to find λ at the particular state at the time t. This assumption is fairly general. As an extreme case it includes the case where the variable λ defines a completely deterministic motion of bath, but in general it may be a coarse-grained description of the microscopic state of the bath.

Now we extend the process of λ to a composite process (λ,ψ) or (λ,ρ) by adding ψ or ρ and consider the joint probability function $P(\lambda,\psi,t)$ or $P(\lambda,\rho,t)$. Then the composite process is also Markoffian and follows the equation

$$\frac{\partial}{\partial t}P(\lambda,\psi,t) =\left\{-\frac{\delta}{\delta\psi}\,\frac{\mathscr{H}(x)\psi}{i\hbar}+\Gamma_\lambda\right\}P(\lambda,\psi,t)\ , \tag{8}$$

or

$$\frac{\partial}{\partial t}P(\lambda,\rho,t) =\left\{-\frac{\delta}{\delta\rho}\,\frac{1}{i\hbar}[\mathscr{H}(x),\rho]+\Gamma_\lambda\right\}P(\lambda,\rho,t)\ . \tag{9}$$

The distribution function $P(\lambda,\psi,t)$ or $P(\lambda,\rho,t)$ gives a full information of the state of the system and the bath. For many purposes it may suffice however to find the expectation

$$\langle\psi(\lambda,t)\rangle=\int\psi P(\lambda,\psi,t)\mathrm{d}\psi\ , \tag{10}$$

or

$$\langle\rho(\lambda,t)\rangle=\int\rho P(\lambda,\rho,t)\ \mathrm{d}\rho\ , \tag{11}$$

for a given state λ of the bath. These are easily found from eq. (8) or (9) to follow the equation

$$\frac{\partial}{\partial t}\langle\psi(\lambda,t)\rangle =\left\{\frac{1}{i\hbar}\mathscr{H}(x)+\Gamma_\lambda\right\}\langle\psi(\lambda,t)\rangle\ , \tag{12}$$

or

$$\frac{\partial}{\partial t}\langle\rho(\lambda,t)\rangle =\frac{1}{i\hbar}[\mathscr{H}(x),\langle\rho(\lambda,t)\rangle]+\Gamma_\lambda\langle\rho(\lambda,t)\rangle\ . \tag{13}$$

These are regarded as generalized equations of motion including the damping effects as induced by the stochastic motion of the bath. These equations may be solved for appropriate initial conditions.

Applications of this approach have been reviewed recently by the present author at a conference in La Jolla and will soon be published.[4] As was mentioned earlier, this treatment ignores the reaction of the system to the bath, or in other words the exchange of energy between the two. This is permissible for instance when the temperature of the bath is sufficiently high compared with the possible energy exchange. Many examples in NMR or Mössbauer effects belong to this category because the reaction to the molecular motion of the bath is extremely small. In optical line-shape problems, similar situations may arise as long as we are interested in the central parts of the spectra where the perturbation mainly comes from distant collisions which do not very much disturb the orbital motion of colliding atoms. Thus the simple stochastic theory as represented by eq. (12) or (13) has a wide range of application to the line-shape problems of NMR, ESR, Mössbauer and optical spectra.[5] The random process governing the change of the Hamiltonian may be assumed in a form appropriate to the problem, or it may be derived from more basic processes underlying in the dynamics of the bath. We shall then be mostly interested in obtaining the understanding how the random modulation will affect the response of the system to external forces.

The basic problems (I) and (II) have to be seriously worried about if the energy exchange is considered. They are still rather simple in classical cases if the linearity of the equation of motion is preserved. Namely, for a free particle or for a harmonic oscillator the Langevin eq. (1) allows some generalizations. The random force $R(t)$ may have a non-white spectrum and correspondingly the friction is retarded or frequency-dependent. Thus eq. (1) may be replaced by

$$\frac{\mathrm{d}p}{\mathrm{d}t}=-\int_0^t \gamma(t-t')\,p(t')\mathrm{d}t'+R(t)\ , \qquad (14)$$

where the retarded friction $\gamma(t)$ must satisfy the fluctuation-dissipation theorem[2]

$$\gamma(t)=\frac{1}{\langle p^2\rangle}\langle R(t)R(0)\rangle\ . \qquad (15)$$

This and the Gaussian assumption for $R(t)$ assure attainment of thermal equilibrium.

In general non-linear cases, the problems become very complicated. For example, consider the Brownian motion of a spin which feels a random local field $\boldsymbol{H}'(t)$. The Langevin equation may be assumed to be[6]

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{M}(t)=\gamma(\boldsymbol{H}_0+\boldsymbol{H}'(t))\times\boldsymbol{M}-\eta\boldsymbol{M}\times(\boldsymbol{M}\times\boldsymbol{H}_0)\ , \qquad (16)$$

where $\boldsymbol{H}_0$ is a constant field and the last term represents the friction in the Landau-Lifshitz type. We note that this equation contains large ambiguities. Only in the limit of extremely fast modulation where the correlation time of $\boldsymbol{H}'(t)$ is short compared with the Zeeman frequency and the mean amplitude of $\boldsymbol{H}'(t)$ itself, eq. (16) leads to an unambiguous result, which may best be represented by an orientational diffusion equation (Fokker-Planck equation) familiar in the classical theory of relaxation of a dipole in a viscous medium.[7] Similarly, eq. (2) may be transformed into a Fokker-Planck equation if the stochastic force $F(a, t)$ has an extremely short correlation time and also satisfies some additional conditions because the details of the stochastic nature of $F(a, t)$ will then become irrelevant. On the other hand, if we want to keep a finite correlation time for $F(a, t)$, the basic questions become very difficult. In eq. (16), for example, what is the right form of the friction term that replaces the one in the equation and guarantees a generalized fluctuation-dissipation theorem? Is the Gaussian assumption for $\boldsymbol{H}'(t)$ really permissible? If so, is there any restriction for its correlation function? These questions cannot easily be answered and in fact they have not been much explored as yet.

Let us turn to quantum-mechanical Brownian motions. The simplest example would be that of a harmonic oscillator, for which one may write the "Langevin" equation,

$$\left.\begin{aligned} b&=i\left(\omega_0+i\frac{1}{2}\gamma\right)b+f(t)\ ,\\ b^*&=-i\left(\omega_0-i\frac{1}{2}\gamma\right)b^*+f^*(t)\ , \end{aligned}\right\} \qquad (17)$$

where b and b^* are the annihilation and creation operators of the oscillator quanta and f and f^* represent the random force. In order to guarantee approach to thermal equilibrium, one assumes that

$$\left.\begin{aligned} \langle f^*(t_1)f(t_2)\rangle&=\gamma\bar{n}\delta(t_1-t_2)\ ,\\ \langle f(t_1)f^*(t_2)\rangle&=\gamma(\bar{n}+1)\delta(t_1-t_2)\ , \end{aligned}\right\} \qquad (18)$$

when $\bar{n}$ is the average quantum number in equilibrium. These assumptions seem to be a natural extension of the fluctuation-dissipation theorem, eq. (4).

A few difficulties are, however, to be noticed immediately. In the first place, unlike the corresponding classical example, the Langevin equation (17) is in fact a very complex object, because the operators f and f^* must contain the dynamics of the bath and so the operator equation (17) are in the operator space of the oscillator and the bath. They are not at all simple as they look.

Secondly, the two equations in (18) are in fact incompatible with each other. It should be remembered that the equation

$$\int_{-\infty}^{\infty}\langle X(0)Y(t)\rangle e^{-i\omega t}dt = e^{\beta\hbar\omega}\int_{-\infty}^{\infty}\langle Y(t)X(0)\rangle e^{-i\omega t}dt\,, \qquad (19)$$

holds generally for two arbitrary quantities X and Y if the average is taken over thermal equilibrium. This means that the spectra of $\langle f^*(t_1)f(t_2)\rangle$ and $\langle f(t_1)f^*(t_2)\rangle$ can never be white at the same time, contrary to the assumption (18). More precisely, the white noise assumption is not permissible for a quantal random force as long as the exchanged energy quanta $\hbar\omega$ have to be kept finite.

The first difficulty may be avoided if the random force is eliminated. This task is achieved by formulating the problem in terms of the density matrix ρ for the Brownian system. A typical procedure of this sort is the derivation of a Bloch-type equation for ρ by treating the interaction between the system and the bath as a perturbation assuming thermal equilibrium of the bath.[8] It should be kept in mind that this corresponds to the Fokker-Planck equation for a classical Brownian system under the assumption of a weak and fast modulation. This approach has been used very widely in various problems. In particular, for the Brownian oscillator one can derive the equation,[9]

$$\frac{\partial\rho}{\partial t}=\frac{1}{i\hbar}[\mathscr{H}_0,\,\rho]+\Gamma_0\rho\,, \qquad (20)$$

$$\Gamma_0\rho=\nu\{[b,\,\rho b^+]+[b\rho,\,b^+]\} + \delta\{[b^+,\,\rho b]+[b^+\rho,\,b]\}\,, \qquad (21)$$

where $\mathscr{H}_0$ is the unperturbed Hamiltonian of the oscillator and Γ_0 represents the incoherent motion of the oscillator caused by the interaction with the bath. The constants ν and δ are related to each other by

$$\delta=\nu e^{-\beta\hbar\omega_0}\,, \qquad (22)$$

which guarantees thermal equilibrium in the steady state.

Equation (20) may be obtained by using the assumptions (18). One should note that the white-noise assumptions (18) do not lead to any contradiction in this particular example because the energy exchange occurs by a definite amount $\pm\hbar\omega_0$. In more general systems, however, this will not be true and the white-noise assumptions can not be maintained.

This fact leads, for example, to difficulties of the following sort. Consider a coupled system of a harmonic oscillator and an atom, which is in contact with a bath only through interaction between the oscillator and the bath. One may be tempted to write an equation like (20) for the density matrix for the oscillator and the atom by using the same form of the incoherent evolution operator Γ_0. This does not guarantee thermal equilibrium and is therefore incorrect. The use of a similar approach is not very unusual.[10] It may not do much harm, however, as long as only high excitations are considered.

As is wellknown, the so-called master equation can be obtained by taking the diagonal part of a Bloch equation. A master equation describes transitions of the system among its quantum states. Equation (19) then gives the condition of the detailed balance, but there remains too great freedom for the possible forms of the transition probabilities unless some idealization is introduced for the properties of the bath. Furthermore, the master equation is incomplete in the sense that it leaves out any information about the coherent part of the evolution of the system.

Concluding this paper, the author would like to repeat that the theory of Brown motion is transparent and complete only for very classical examples. Once when we start to go beyond the restrictions, which brought such a beauty to the classical theory, we encounter a number of difficulties. These difficulties are concealed in disguised forms in any method treating a many-body system. It will be thus important for the future of the statistical physics to develop collaboration of two lines of approach, one from the microscopic side and the other from a phenomenological side.

References

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DISCUSSION

N. G. van Kampen: The difficulty you mentioned in the last few minutes does not seem so serious to me. The Langevin equation with the usual stochastic properties of the Langevin force can only be believed for appropriate macroscopic quantities anyway. In other words, it is only true on a coarse-grained level, where questions of commutability are already irrelevant. I cannot formulate this remark is precise terms, but I do not see a prima facie paradox.

R. Kubo: I agree with you in that the Langevin equation is all right as long as it is used for a macroscopic system. However, one would like to see how the Langevin equation is extended to quantum-mechanical systems. For example to an oscillator or an atom in contact with a bath. This you will see in the example of quantum noise problems which have been discussed by Lax, Haken and other investigators. When you write for example an equation like

$$\dot{b}=\left(i\omega_0-\frac{\gamma}{2}\right)b+f(t) \ ,$$

as Lax does, you should notice first that the random force $f(t)$ must be an operator in a space different from the Hilbert space of the oscillator. On the other hand, you want after all formulate the problem in the space of the oscillator (or the system you are concerned with). That means that the random force is going to be eliminated, and in this elimination, only the stochastic characteristics of $f(t)$ is used. In classical mechanics, there is no difficulty in the idealization of $f(t)$ as a white noise. In quantum-mechanics this is not possible. We would like to find a simplest possible form of random force which can be used an idealization of a bath. But it is no simple problem. For an oscillator or for an atom you can find some simplication, and write the equation of motion of a density matrix in the form

$$\frac{\partial\rho}{\partial t}=\frac{1}{i\hbar}[\mathscr{H}_0, \rho]+\Gamma_0\rho \ ,$$

where $\Gamma_0\rho$ represents the incoherent motion. In connection with the difficulty, mentioned above, it should be kept in mind that this incoherent parts cannot be superposed. That is, for instance, when you have an oscillator and an atom coupled to each other you just cannot add Γ_0 and Γ_a for the oscillator and the atom even when each separately is in contact with its own bath.