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On the derivation of the fluctuation–dissipation theorem

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Abstract. We give a critical analysis of a derivation due to Kubo of the fluctuation–dissipation theorem for classical systems. It is shown that a basic assumption having the appearance of a causality condition actually should be understood as an incidental corollary of the equations.

1. Introduction

Some years ago Kubo (1966) gave a very interesting derivation of the fluctuation–dissipation theorem for classical systems. Using as an example the Brownian motion of a particle with a retarded friction coefficient he derived the theorem from a minimum of assumptions. Since these assumptions appeared self-evident he seemed to have achieved a derivation which obviated postulating the theorem on the basis of a generalised Onsager hypothesis.

Kubo defined the random force $R(t)$ acting on the Brownian particle relative to a chosen initial time, say $t=0$. One of his assumptions reads

$$\langle R(t)u(0)\rangle = 0, \qquad t>0, \tag{1.1}$$

where $u(0)$ is the velocity of the particle at time $t=0$. This equation has the appearance of a causality condition and seems self-evident. Though we do not doubt its validity we shall argue that this equation is not fundamental and should rather be considered as a corollary. We regard the fluctuation–dissipation theorem as a basic postulate of non-equilibrium statistical mechanics and contend that it cannot be derived from more fundamental principles.

2. Kubo's derivation of the fluctuation–dissipation theorem

The equation of motion for the average velocity of a Brownian particle in one dimension reads

$$m\langle \dot{u}(t)\rangle + m\int_{-\infty}^{t} \gamma(t-t')\langle u(t')\rangle \, dt' = K(t), \tag{2.1}$$

where m is the mass of the particle, $u(t)$ its velocity, $\gamma(t-t')$ represents the retarded effect of the frictional force, and $K(t)$ is the external force. In terms of Fourier

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transforms

$$u_\omega = \frac{1}{2\pi}\int_{-\infty}^{\infty} u(t)\, e^{i\omega t}\, dt, \qquad K_\omega = \frac{1}{2\pi}\int_{-\infty}^{\infty} K(t)\, e^{i\omega t}\, dt, \tag{2.2}$$

equation (2.1) becomes

$$\langle u_\omega \rangle = Y(\omega) K_\omega \tag{2.3}$$

where the admittance $Y(\omega)$ is given by

$$Y(\omega) = \frac{1}{m}\frac{1}{-i\omega + \hat{\gamma}(\omega)} \tag{2.4}$$

with

$$\hat{\gamma}(\omega) = \int_0^{\infty} e^{i\omega t}\, \gamma(t)\, dt. \tag{2.5}$$

Kubo (1966) considers the following generalised Langevin equation for the stochastic motion of the particle:

$$m\dot{u}(t) + m\int_0^t \gamma(t-t')u(t')\, dt' = K(t) + R(t), \qquad t > 0, \tag{2.6}$$

where $R(t)$ is the random force. About the random force he assumes that it averages to zero,

$$\langle R(t) \rangle = 0, \tag{2.7}$$

that for $t > 0$ it is not correlated with the velocity $u(0)$,

$$\langle R(t) u(0) \rangle = 0, \qquad t > 0, \tag{2.8}$$

and that it does not depend on the external force K. Furthermore he assumes that in the absence of the external force the stochastic process $u(t)$ is stationary, i.e. for $K(t) = 0$ the correlation function

$$\Psi(\tau) = \langle u(t+\tau) u(t) \rangle \tag{2.9}$$

does not depend on t. Finally he uses the equilibrium variance

$$\langle u^2 \rangle = kT/m. \tag{2.10}$$

From equations (2.6)–(2.8) one finds

$$\hat{\Psi}(\omega) \equiv \int_0^{\infty} e^{i\omega\tau}\Psi(\tau)\, d\tau = \langle u^2 \rangle \frac{1}{-i\omega + \hat{\gamma}(\omega)}, \tag{2.11}$$

so that, using equations (2.4) and (2.10),

$$\hat{\Psi}(\omega) = kTY(\omega). \tag{2.12}$$

Kubo calls this the first fluctuation–dissipation theorem. Using the stationarity of the stochastic process $u(t)$ he goes on to show that

$$\int_0^{\infty} e^{i\omega\tau}\langle R(\tau) R(0) \rangle\, d\tau = kTm\hat{\gamma}(\omega), \tag{2.13}$$

which he calls the second fluctuation–dissipation theorem.

Equations (2.12) and (2.13) can be regarded as expressions for the correlation functions of the velocity and the random force in terms of the macroscopic friction coefficient. Conversely they can be used to evaluate the friction coefficient if the correlation functions can be calculated from a microscopic theory. The equations have been derived with a minimum of assumptions.

3. Nyquist's theorem

We contrast the derivation of equations (2.12) and (2.13) to similar equations obtained by postulating the validity of Nyquist's theorem (Nyquist 1928). In writing equation (2.6) one has broken the time-translation invariance of the description and the random force $R(t)$ is defined with respect to the chosen time $t=0$. The proper time-translation invariant generalisation of equation (2.1) is given by

$$m\dot{u}(t)+m\int_{-\infty}^{t}\gamma(t-t')u(t')\,\mathrm{d}t'=K(t)+L(t), \tag{3.1}$$

where $L(t)$ is the stochastic or Langevin force (denoted as $R'(t)$ by Kubo). It is related to the random force $R(t)$ by

$$R(t)=L(t)-m\int_{-\infty}^{0}\gamma(t-t')u(t')\,\mathrm{d}t'. \tag{3.2}$$

In order to apply Nyquist's theorem one must first verify that $u(t)$ and $K(t)$ occur as a pair of conjugate variables in the energy dissipated by the system. The energy absorbed by the system up to time t under the influence of the external force $K(t)$ on the average is given by

$$P(t)=\int_{-\infty}^{t}\langle u(t')\rangle K(t')\,\mathrm{d}t'. \tag{3.3}$$

The statement that this is positive for all t, and that $\langle u(t)\rangle$ and $K(t)$ are linearly related defines a linear passive system implying certain analyticity properties of the admittance $Y(\omega)$ in the complex ω-plane (Meixner 1965). In the absence of the external force $K(t)$ the fluctuating velocity and the stochastic force are related by

$$u_\omega=Y(\omega)L_\omega, \tag{3.4}$$

as follows from equation (3.1). According to Nyquist's (1928) theorem the spectrum of the stochastic force is given by

$$\langle L_\omega L^*_{\omega'}\rangle=\frac{kT}{\pi}\operatorname{Re}Z(\omega)\delta(\omega-\omega'), \tag{3.5}$$

where $Z(\omega)$ is the impedance, which is the inverse of the admittance,

$$Y(\omega)Z(\omega)=1. \tag{3.6}$$

From equations (3.4) and (3.5) it follows that the spectrum of the velocity fluctuations is given by

$$\langle u_\omega u^*_{\omega'}\rangle=\frac{kT}{\pi}\operatorname{Re}Y(\omega)\delta(\omega-\omega'). \tag{3.7}$$

If we write these spectra in the form

$$\langle L_\omega L^*_{\omega'}\rangle = S_{LL}(\omega)\delta(\omega-\omega'), \qquad \langle u_\omega u^*_{\omega'}\rangle = S_{uu}(\omega)\delta(\omega-\omega'), \tag{3.8}$$

then according to the Wiener–Khinchin theorem the functions $S_{LL}(\omega)$ and $S_{uu}(\omega)$ are the Fourier transforms of the time correlation functions

$$S_{LL}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle L(t+\tau)L(t)\rangle\, \mathrm{e}^{\mathrm{i}\omega\tau}\,\mathrm{d}\tau, \tag{3.9a}$$

$$S_{uu}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle u(t+\tau)u(t)\rangle\, \mathrm{e}^{\mathrm{i}\omega\tau}\,\mathrm{d}\tau. \tag{3.9b}$$

Equations (3.7) and (3.9b) are equivalent to equation (2.12). We note that equation (2.10) follows from (2.12) by considering (3.6) for large ω. From equations (3.5) and (3.9a) it follows by use of (2.4) and (3.6) that

$$\int_0^{\infty}\mathrm{e}^{\mathrm{i}\omega\tau}\langle L(t+\tau)L(t)\rangle\,\mathrm{d}\tau = mkT\hat{\gamma}(\omega). \tag{3.10}$$

Using the definition (3.2) of the random force and equation (2.12) one hence derives (2.13). Thus one has

$$\langle L(t+\tau)L(t)\rangle = \Gamma(\tau) = \langle R(\tau)R(0)\rangle \tag{3.11}$$

with

$$\Gamma(\tau) = mkT\gamma(|\tau|). \tag{3.12}$$

In this section the correlation functions of the stochastic force and of the velocity have been obtained by postulate rather than by derivation. The Nyquist theorem must be regarded as a generalised Onsager hypothesis. This hypothesis can be circumvented by the minimum of assumptions formulated in the preceding section. In the sequel we shall argue, however, that equation (2.8) is less fundamental than it appears to be.

4. Deductions from Nyquist's theorem

We can draw further conclusions from the spectra postulated in the preceding section. The defining equation (3.2) for the random force $R(t)$ can be written for $K(t)=0$

$$R(t) = m\dot{u}(t) + m\int_0^t \gamma(t-t')u(t')\,\mathrm{d}t'. \tag{4.1}$$

We regard this as a definition of $R(t)$ for both positive and negative t with $\gamma(-t)=\gamma(t)$. One now shows straightforwardly by use of equations (2.10) and (2.12)

$$\langle R(t)u(0)\rangle = 0, \qquad \text{for all } t. \tag{4.2}$$

Thus equation (2.8), which derives a certain plausibility from its appearance as a statement of causality, is in fact only part of equation (4.2) and the latter equation for $t<0$ has no intuitive appeal.

Using equation (4.1) one can express the time correlation function $\langle R(t+\tau)R(t)\rangle$ in terms of $\langle u(t+\tau)u(t)\rangle$. Surprisingly, if one evaluates the derivative of $\langle R(t+\tau)R(t)\rangle$

with respect to t one finds that it vanishes. Hence one has, using equation (3.11),

$$\langle R(t+\tau)R(t)\rangle = \Gamma(\tau), \tag{4.3}$$

which makes it appear that $R(t)$ is a stationary random process. In fact, of course, it is not, as one sees by forming the time derivative

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle R(t+\tau)u(t)\rangle = \beta\Gamma(t+\tau)\Psi(t), \tag{4.4}$$

where $\beta = 1/kT$. From equations (4.2) and (4.4) it follows that

$$\langle R(t+\tau)u(t)\rangle = \beta\int_0^t \Gamma(t'+\tau)\Psi(t')\,\mathrm{d}t'. \tag{4.5}$$

Hence equation (4.2) appears as a somewhat fortuitous corollary of the definition (4.1) of the random force $R(t)$. If one evaluates the time correlation of the stochastic force $L(t)$ with $u(t)$ one finds

$$\langle L(t+\tau)u(t)\rangle = \beta\int_0^\infty \Gamma(t'+\tau)\Psi(t')\,\mathrm{d}t' \tag{4.6}$$

independent of t. For large t the random force $R(t)$ becomes a stationary process and equation (4.5) reduces to (4.6).

5. Extension to bound particle and more dimensions

The theory is easily extended to the case where the particle is bound. In the linear theory the binding potential is approximated by an harmonic one. The stochastic equation of motion (3.1) now becomes

$$m\dot{u}(t) + m\omega_0^2 x(t) + m\int_{-\infty}^t \gamma(t-t')u(t')\,\mathrm{d}t = K(t) + L(t). \tag{5.1}$$

The impedance is now given by

$$Z(\omega) = -\mathrm{i}\omega m - \frac{m\omega_0^2}{\mathrm{i}\omega} + m\hat{\gamma}(\omega). \tag{5.2}$$

Considering the identity (3.6) in the limit $\omega \to 0$ and using equation (2.12) one finds

$$\langle x^2\rangle = kT/m\omega_0^2 \tag{5.3}$$

which complements equation (2.10). The fluctuation spectra of the stochastic force and of the velocity are again given by equations (3.5) and (3.7) and one easily checks that with the modified definition of the random force,

$$R(t) = m\dot{u}(t) + m\omega_0^2 x(t) + m\int_0^t \gamma(t-t')u(t')\,\mathrm{d}t' \tag{5.4}$$

all proofs of the preceding section remain valid. In addition one shows that

$$\langle R(t)x(0)\rangle = 0, \qquad \text{for all } t. \tag{5.5}$$

In the generalisation to more dimensions it is convenient to consider variables $\boldsymbol{x}(t)$ with zero thermal average, $\langle \boldsymbol{x}\rangle = 0$, and to define corresponding velocities $\boldsymbol{u}(t) = \dot{\boldsymbol{x}}(t)$.

The generalised equation of motion becomes

$$\mathbf{A}\cdot\dot{\boldsymbol{u}}(t)+\mathbf{B}\cdot\boldsymbol{x}(t)+\beta\int_{-\infty}^{t}\boldsymbol{\Gamma}(t-t')\cdot\boldsymbol{u}(t')\,\mathrm{d}t'=\boldsymbol{K}(t)+\boldsymbol{L}(t). \tag{5.6}$$

For the application of Nyquist's theorem one must check that $\langle\boldsymbol{u}(t)\rangle$ and $\langle\boldsymbol{K}(t)\rangle$ appear as conjugate variables in the energy dissipation, as in equation (3.3). The impedance matrix becomes

$$\mathbf{Z}(\omega)=\mathrm{i}\omega\mathbf{A}-\frac{\mathbf{B}}{\mathrm{i}\omega}+\beta\hat{\boldsymbol{\Gamma}}(\omega), \tag{5.7}$$

and its inverse is the admittance matrix $\mathbf{Y}(\omega)=\mathbf{Z}(\omega)^{-1}$. The Nyquist theorem for the stochastic force and for the fluctuating velocities in the absence of the external force $\boldsymbol{K}(t)$ now reads

$$\begin{aligned}\langle\boldsymbol{L}_\omega\boldsymbol{L}^*_{\omega'}\rangle&=\frac{kT}{2\pi}(\mathbf{Z}(\omega)+\mathbf{Z}(\omega)^\dagger)\delta(\omega-\omega'),\\ \langle\boldsymbol{u}_\omega\boldsymbol{u}^*_{\omega'}\rangle&=\frac{kT}{2\pi}(\mathbf{Y}(\omega)+\mathbf{Y}(\omega)^\dagger)\delta(\omega-\omega').\end{aligned} \tag{5.8}$$

As before one shows that the matrices $\mathbf{A}$ and $\mathbf{B}$ are related to the equilibrium fluctuations by

$$\mathbf{A}=kT\langle\boldsymbol{uu}\rangle^{-1},\qquad \mathbf{B}=kT\langle\boldsymbol{xx}\rangle^{-1}. \tag{5.9}$$

It is easily checked that with the definition of the random force

$$\boldsymbol{R}(t)=\mathbf{A}\cdot\dot{\boldsymbol{u}}(t)+\mathbf{B}\cdot\boldsymbol{x}(t)+\beta\int_{0}^{t}\boldsymbol{\Gamma}(t-t')\cdot\boldsymbol{u}(t')\,\mathrm{d}t', \tag{5.10}$$

with $\boldsymbol{\Gamma}(-t)=\tilde{\boldsymbol{\Gamma}}(t)$, the previous proofs can be carried through in matrix notation.

Finally, we note that the equations can be rewritten to fit the framework of the Mori formalism (Mori 1965). The random force which occurs in Mori's theory is defined in terms of the microscopic Hamiltonian equations of motion. It can be shown to have the properties we have derived above.

6. Conclusion

In our opinion Kubo's derivation of the fluctuation–dissipation theorem as sketched in § 2 is deceptively simple. The basic assumption (equation (2.8)) appears plausible as it seems to express a causality property. As we have shown, it must be regarded as part of equation (4.2) and thereby loses its intuitive appeal. The proper Langevin force $L(t)$, which is a realisation of a stationary random process in contrast to the random force $R(t)$, does have correlations with the velocity at previous times, as shown explicitly in equation (4.6). We regard equation (2.8) as an incidental corollary to which no great significance should be attached. The statement that the equilibrium time correlation functions for the fluctuations can be expressed in terms of the coefficients occurring in the macroscopic equations is a fundamental assumption of statistical mechanics and is to be regarded as a generalised Onsager hypothesis. We feel that from a didactic point of view the fluctuation–dissipation theorem is best made plausible by means of a simple model system, as treated, for example, by Becker (1967).

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