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Linear-response theory and the fluctuation-dissipation theorem: An executive summary

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• LINEAR-RESPONSE PHENOMENOLOGY

If $A(t)$ is an externally controlled variable and $B(t)$ the measured "response" and equilibrium corresponds to $A = 0$ and $B = 0$, **linearity** implies

$$B(t) \;=\; \int_{-\infty}^{\infty} \phi(t,\tau) A(t-\tau) d\tau\,. \tag{1}$$

Causality further implies

$$B(t) \;=\; \int_{0}^{\infty} \phi(t,\tau) A(t-\tau) d\tau\,. \tag{2}$$

Time-translational invariance finally implies

$$B(t) \;=\; \int_{0}^{\infty} \phi(\tau) A(t-\tau) d\tau\,. \tag{3}$$

In steady-state periodic fields one writes $A(t) = \mathrm{Re}[A(\omega)\exp(i\omega t)]$ and $B(t) = \mathrm{Re}[B(\omega)\exp(i\omega t)]$. Equation (3) implies $B(\omega) = \phi(\omega)A(\omega)$ where (exercise 4)

$$\phi(\omega) \;=\; \int_{0}^{\infty} \phi(t) e^{-i\omega t} dt\,. \tag{4}$$

• ENERGY BONDS

Any energetic interaction between a system and its surroundings defines an *energy bond.* If $e(t)$ is the "effort" (generalized force) and $f(t)$ is the "flow" (generalized velocity), the product $e(t)f(t)$ is the power transferred from the surroundings to the system, i.e., energy per unit time. Throughout this note we shall assume (what is usually the case) that the effort variable is invariant under time reversal whereas the flow variable changes sign.

- **FLUCTUATION-DISSIPATION THEOREM**

If the effort is externally controlled, the measured flow response $\langle f(t)\rangle_e$ is given by

$$\langle f(t)\rangle_e \;=\; \frac{1}{k_BT}\int_0^\infty \langle f(0)f(\tau)\rangle_0 e(t-\tau)d\tau\,. \tag{5}$$

In principle the measured response is an average, thus the sharp brackets on the left-hand side. In Eq. (5) subscript zero signals that the flow autocorrelation function refers to *equilibrium* conditions, i.e., $e=0$. If the flow is externally controlled, the average measured effort response $\langle e(t)\rangle_f$ is given by

$$\langle e(t)\rangle_f \;=\; \frac{1}{k_BT}\int_0^\infty \langle e(0)e(\tau)\rangle_0 f(t-\tau)d\tau\,. \tag{6}$$

Note that the two equilibrium conditions, $e=0$ and $f=0$ respectively, usually correspond to different physical boundary conditions.

- **GENERALIZED ADMITTANCE AND IMPEDANCE**

It follows from the above that the generalized admittance describing the periodic situation $Y(\omega)\equiv f(\omega)/e(\omega)$ is given by

$$Y(\omega) \;=\; \frac{1}{k_BT}\int_0^\infty \langle f(0)f(\tau)\rangle_0 e^{-i\omega\tau}d\tau\,. \tag{7}$$

The generalized impedance $Z(\omega)\equiv e(\omega)/f(\omega)$ is given by

$$Z(\omega) \;=\; \frac{1}{k_BT}\int_0^\infty \langle e(0)e(\tau)\rangle_0 e^{-i\omega\tau}d\tau\,. \tag{8}$$

- **CREEP FUNCTION FORMULATION OF THE FLUCTUATION-DISSIPATION THEOREM**

If q is the generalized displacement defined by $\Delta q(t)\equiv\int_0^t f(\tau)d\tau$, the creep function $J(t)$ characterizes the generalized displacement in time t when a constant effort e_0 is suddenly applied to the system at time $t=0$: $J(t)\equiv\langle\Delta q(t)\rangle_{e_0}/e_0$. In terms of the equilibrium mean-square displacement, the fluctuation-dissipation theorem expresses the creep function as follows (exercise 9):

$$J(t) \;=\; \frac{\langle\Delta q^2(t)\rangle_0}{2k_BT}\,. \tag{9}$$

- **SEVERAL ENERGY BONDS: ONSAGER RECIPROCITY**

In the case of n energy bonds the fluctuation-dissipation theorem looks as follows:

$$\langle f_i(t)\rangle_e \;=\; \frac{1}{k_BT}\sum_{j=1}^{n}\int_0^\infty \langle f_i(0)f_j(\tau)\rangle_0 e_j(t-\tau)d\tau\,. \tag{10}$$

Similarly when flows are externally controlled:

$$\langle e_i(t)\rangle_f \;=\; \frac{1}{k_B T}\sum_{j=1}^{n}\int_0^\infty \langle e_i(0)e_j(\tau)\rangle_0 f_j(t-\tau)d\tau\,. \tag{11}$$

Mixed cases where some efforts and other flows are externally controlled may also be considered. Usually one chooses one variable from each energy bond as externally controlled and the other becomes a response variable, but this is not mandatory; any n of the $2n$ variables may be chosen as controlled. − Time-reversal invariance of the fundamental equations of motion (the Schrodinger equation / Newton's equation of motion) implies the following symmetries:

$$\langle f_i(0)f_j(\tau)\rangle_0 \;=\; \langle f_j(0)f_i(\tau)\rangle_0\,, \tag{12}$$

and

$$\langle e_i(0)e_j(\tau)\rangle_0 \;=\; \langle e_j(0)e_i(\tau)\rangle_0\,. \tag{13}$$

For the generalized admittance and impedance matrices these identities imply symmetry of the response matrices (Onsager reciprocity): $Y_{ij}(\omega) = Y_{ji}(\omega)$ and $Z_{ij}(\omega) = Z_{ji}(\omega)$.

EXERCISES

1: Consider a particle moving in the one-dimensional potential $U_0(x) = \alpha x^2/2$. Show that for the thermal average one has $\langle x^2 \rangle_0 = k_B T/\alpha$. Next an external field h is coupled to the system, thus the potential is modified into $U(x) = U_0(x) - hx$. The average of x becomes a function of the field, denoted by $\langle x \rangle_h$. Show that

$$\left.\frac{\partial \langle x \rangle_h}{\partial h}\right|_{h=0} = \frac{\langle x^2 \rangle_0}{k_B T}\,. \tag{14}$$

2: Consider now an arbitrary potential $U_0(x)$. Show that if $U(x) = U_0(x) - hx$, Eq. (14) generalizes into

$$\left.\frac{\partial \langle x \rangle_h}{\partial h}\right|_{h=0} = \frac{\langle (\Delta x)^2 \rangle_0}{k_B T}\,. \tag{15}$$

Hint: Define $Z \equiv \int_{-\infty}^{\infty} \exp[-\beta U(x)]dx$ where $\beta \equiv 1/k_B T$. Show that $\langle x \rangle_h = \beta^{-1}\partial \ln Z/\partial h$ and $\langle (\Delta x)^2 \rangle_0 = \beta^{-2}\partial^2 \ln Z/\partial h^2|_{h=0}$.

3: Derive Eq. (4).

4: Out of a black box come two electrical wires. The voltage across the wires is denoted by $U(t)$, the current through the black box by $I(t)$. Identify the effort and flow variables and write an expression for the impedance $Z(\omega)$ in terms of the voltage fluctuations across the black box when there is no current [Nyquist theorem].

5: Consider a particle in one dimension experiencing a force $F(x)$ deriving from a (possibly) non-linear spring. What are the effort and flow variables in this case?

6: A liquid is immersed between two parallel plates with area A of distance d, volume $V = Ad$. The lower plate is fixed to a table; the upper plate experiences an external force parallel to the table. Identify the effort and flow variables and write an expression for the (dc) viscosity in terms of the force autocorrelation function for the case where the upper plate is not allowed to move. *Extra:* Rewrite this expression in terms of the following variable $S_{xz} \equiv \int_V d\mathbf{r}\sigma_{xz}(\mathbf{r})$.

7: As is well known, most of thermodynamics may be derived from the identity $TdS = dE + pdV$ that contains both the first and second law. Identify the effort and flow variables for the thermal and mechanical energy bonds to a general thermodynamic system, respectively, referring to the case of small perturbations around equilibrium.

8: Derive the Kubo formula for the frequency-dependent conductivity

$$\sigma(\omega) = \frac{1}{V k_B T}\int_0^{\infty} \langle J_x(0) J_x(t)\rangle_0 e^{-i\omega t} dt \tag{16}$$

where V is the sample volume and J_x is the sum of charge times x-velocity for all particles. What is the boundary condition for the autocorrelation function? *Extra:* Express the frequency-dependent dielectric constant in terms of the dipole autocorrelation function.

9: Derive Eq. (9).

10: Derive the Nernst-Einstein relation for non-interacting charge carriers, $\mu = D/k_B T$ where μ is the mobility (average velocity over external force) and D the diffusion constant characterized by Einstein's equation $\langle (\Delta x)^2(t) \rangle_0 = 2Dt$ as $t \to \infty$.

REFERENCES

Nowadays any advanced text on statistical mechanics treats the fluctuation-dissipation theorem. My favourites are rather old books:

R. Becker, *Theory of Heat* (Springer, Berlin, 1967). This book is a masterpiece for all of thermal physics. One of the last chapters deals with fluctuations from a rather historical viewpoint. Going through this is an excellent way to be introduced to various special cases of the fluctuation-dissipation theorem.

M. Doi and S. F. Edwards, *Dynamics of Polymeric Liquids* (Cambridge University Press, 1986). The fluctuation-dissipation theorem for the important case of stochastic dynamics is derived on a few pages with Edwards' typical elegance.

L. D. Landau and E. M. Lifshitz, 1969, *Statistical Physics*, 2nd Ed. (Pergamon, Oxford, 1969). The 10-volume textbook series by Landau and Lifshitz are among the best physics books, though not necessarily easy to learn a new subject from. These books are unique in the history of physics and are highly recommended as supplementing more elementary approaches. This applies also for the fluctuation-dissipation theorem that is treated in part by adopting the noise-spectrum approach going back to the seminal papers by Nyquist and Johnson from the 1920's (though in a modern setting including all the quantum complications we ignored here).

L. E. Reichl, *A Modern Course in Statistical Physics* 2nd Ed. (Wiley, New York, 1998). This comprehensive book contains basically "all you always wanted to know and were afraid to ask" regarding statistical physics.

N. G. Van Kampen, *Stochastical Processes in Physics and Chemistry* (North Holland, Amsterdam, 1981). A remarkably concise, mathematically precise and well-written textbook; every single sentence appears to be carefully considered.

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G. N. Bochkov and Yu. E. Kuzovlev, Physica **106A**, 443 (1981); **106A**, 480 (1981). These two important papers derive what in the 1990's became known as the "fluctuation theorem", a non-linear generalization of the fluctuations-dissipation theorem derived solely from the time-reversal invariance of the fundamental equations of motion. The first part of the first paper gives a beautifully simple proof of the ordinary (linear) fluctuation-dissipation theorem.

An example of how the method of Doi and Edwards may be applied to derive the fluctuation-dissipation theorem for the frequency-dependent specific heat is given in the following paper: J. K. Nielsen and J. C. Dyre, Phys. Rev. B **54**, 15754 (1996).