

Statistical Physics of Athermal Systems

Lecture 2

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1 Recap

At the end of Lecture 1 we had eliminated the bath degrees of freedom from a Hamiltonian system and obtained the generalized Langevin equation

$$m\ddot{q}(t) + V'(q(t)) + \int_0^t ds \Gamma(t-s)\dot{q}(s) = \eta(t), \quad (1)$$

where, for the mass-normalized Caldeira–Leggett bath,

$$\Gamma(t) = \sum_a \frac{c_a^2}{\omega_a^2} \cos(\omega_a t), \quad (2)$$

and the random force is the force exerted by the bath's initial conditions. The key point is that Eq. (1) by itself is not yet a thermal equation. It contains a deterministic memory kernel and a fluctuating force, but their relation has not been used. The equilibrium statement enters only when the bath is prepared in a Gibbs state. Then the same microscopic bath that produces dissipation also fixes the amplitude and temporal structure of the fluctuations. Recall the convenient shifted coordinates

$$y_a = x_a - \frac{c_a}{\omega_a^2} q(0). \quad (3)$$

For fixed $q(0)$, the bath Hamiltonian is a collection of independent harmonic oscillators,

$$H_{\text{bath}}^{\text{shifted}} = \sum_a \left[\frac{\pi_a^2}{2} + \frac{\omega_a^2 y_a^2}{2} \right]. \quad (4)$$

If the bath is at temperature T , the initial distribution is Gaussian and factorized. Equipartition gives

$$\langle y_a(0) \rangle = 0, \quad \langle \pi_a(0) \rangle = 0, \quad (5)$$

$$\langle y_a(0) y_b(0) \rangle = \frac{k_B T}{\omega_a^2} \delta_{ab}, \quad \langle \pi_a(0) \pi_b(0) \rangle = k_B T \delta_{ab}, \quad (6)$$

$$\langle y_a(0) \pi_b(0) \rangle = 0. \quad (7)$$

The fluctuating force can be written entirely in terms of the shifted variables,

$$\eta(t) = \sum_a c_a \left[y_a(0) \cos(\omega_a t) + \frac{\pi_a(0)}{\omega_a} \sin(\omega_a t) \right]. \quad (8)$$

Its mean is immediately zero:

$$\langle \eta(t) \rangle = 0. \quad (9)$$

2 Fluctuation–dissipation

2.1 Spectral density of the Caldeira–Leggett bath

For a large bath, the discrete mode sum is naturally expressed through the spectral density

$$\mathcal{J}(\omega) = \frac{\pi}{2} \sum_a \frac{c_a^2}{\omega_a} \delta(\omega - \omega_a), \quad \omega > 0. \quad (10)$$

With this convention,

$$\Gamma(t) = \sum_a \frac{c_a^2}{\omega_a^2} \cos(\omega_a t) \quad (11)$$

$$= \frac{2}{\pi} \int_0^\infty d\Omega \frac{\mathcal{J}(\Omega)}{\Omega} \cos(\Omega t). \quad (12)$$

Fourier conventions: throughout this lecture we use

$$A(\omega) = \int_{-\infty}^\infty dt e^{i\omega t} A(t), \quad (13)$$

$$A(t) = \int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{-i\omega t} A(\omega). \quad (14)$$

With these conventions,

$$\int_{-\infty}^\infty dt e^{i\omega t} \cos(\Omega t) = \pi [\delta(\omega - \Omega) + \delta(\omega + \Omega)]. \quad (15)$$

Therefore the two-sided Fourier transform of the memory kernel is

$$\tilde{\Gamma}(\omega) \equiv \int_{-\infty}^\infty dt e^{i\omega t} \Gamma(t) = \frac{2\mathcal{J}(|\omega|)}{|\omega|}, \quad \omega \neq 0. \quad (16)$$

The noise spectral density is defined by

$$S_{\eta\eta}(\omega) = \int_{-\infty}^\infty dt e^{i\omega t} \langle \eta(t) \eta(0) \rangle. \quad (17)$$

Using the noise correlation, we arrive at

$$S_{\eta\eta}(\omega) = k_B T \tilde{\Gamma}(\omega) = \frac{2k_B T}{|\omega|} \mathcal{J}(|\omega|). \quad (18)$$

This is the frequency-domain form of FDT.

2.2 The Ohmic limit and white noise

An Ohmic bath has

$$\mathcal{J}(\omega) = \gamma \omega f(\omega/\omega_c), \quad (19)$$

where f is a high-frequency cutoff function and $f(0) = 1$. In the broad-band limit, the cutoff is far above all frequencies relevant to the system. Then

$$\mathcal{J}(\omega) \simeq \gamma \omega, \quad (20)$$

and hence

$$\Gamma(t) \rightarrow 2\gamma\delta(t). \quad (21)$$

Because the friction term is a one-sided convolution, the boundary convention produces the usual local damping term,

$$\int_0^t ds \Gamma(t-s)\dot{q}(s) \rightarrow \gamma\dot{q}(t). \quad (22)$$

At the same time,

$$S_{\eta\eta}(\omega) \rightarrow 2\gamma k_B T, \quad (23)$$

which is independent of frequency. Thus the Markovian noise is white:

$$\langle \eta(t)\eta(t') \rangle = 2\gamma k_B T \delta(t-t'). \quad (24)$$

The cutoff is important physically: an exactly flat noise spectrum extending to arbitrarily high frequency is an idealization.

2.3 Linear response and the retarded susceptibility

We now derive the relation between a measurable response and an unperturbed fluctuation. Let

$$H_h(t) = H_0 - h(t)A, \quad (25)$$

where A is the observable conjugate to the external field h . We measure an observable B . Linear response defines

$$\delta \langle B(t) \rangle = \int_{-\infty}^t dt' R_{BA}(t-t')h(t'). \quad (26)$$

Causality requires

$$R_{BA}(t) = 0, \quad t < 0. \quad (27)$$

For a stationary equilibrium state, the response depends only on the time difference. We define the susceptibility

$$\chi_{BA}(\omega) = \int_0^\infty dt e^{i\omega t} R_{BA}(t). \quad (28)$$

Write

$$\chi_{BA}(\omega) = \chi'_{BA}(\omega) + i\chi''_{BA}(\omega). \quad (29)$$

The imaginary part is the dissipative or out-of-phase response. Causality alone gives the Kramers–Kronig relations; equilibrium will provide the additional relation to fluctuations.

2.4 Detailed balance

The fluctuation–dissipation theorem is not a consequence of the Boltzmann weight alone. The crucial dynamical ingredient is microscopic reversibility, expressed for stochastic dynamics by detailed balance. It is useful to make this statement explicit before deriving FDT. For an overdamped system with

$$\gamma\dot{q}_i = -\frac{\partial V}{\partial q_i} + \eta_i(t), \quad \langle \eta_i(t)\eta_j(t') \rangle = 2\gamma k_B T \delta_{ij}\delta(t-t'), \quad (30)$$

the Fokker–Planck equation is

$$\frac{\partial P}{\partial t} = \sum_i \frac{\partial}{\partial q_i} \left[\frac{\partial V}{\partial q_i} P + k_B T \frac{\partial P}{\partial q_i} \right] \frac{1}{\gamma}. \quad (31)$$

Writing it as a continuity equation,

$$\frac{\partial P}{\partial t} = - \sum_i \frac{\partial J_i}{\partial q_i}, \quad (32)$$

the probability current is

$$J_i = -\frac{1}{\gamma} \left[\frac{\partial V}{\partial q_i} P + k_B T \frac{\partial P}{\partial q_i} \right]. \quad (33)$$

The Gibbs distribution

$$P_{\text{eq}} = \frac{1}{Z} e^{-\beta V} \quad (34)$$

makes every current vanish individually:

$$\frac{\partial P_{\text{eq}}}{\partial q_i} = -\beta \frac{\partial V}{\partial q_i} P_{\text{eq}}, \quad (35)$$

and hence

$$J_i^{\text{eq}} = 0. \quad (36)$$

This is detailed balance: equilibrium is not merely stationary,

$$\partial_t P_{\text{eq}} = 0, \quad (37)$$

but has no probability circulation through configuration space. For a transition process with rates $W_{a \rightarrow b}$, the same statement is

$$P_{\text{eq}}(a) W_{a \rightarrow b} = P_{\text{eq}}(b) W_{b \rightarrow a}. \quad (38)$$

Thus every elementary transition is balanced by its reverse. For a trajectory

$$a_0 \rightarrow a_1 \rightarrow \cdots \rightarrow a_n, \quad (39)$$

multiplying Eq. (38) along the path gives

$$\frac{\mathcal{P}[\text{forward path}]}{\mathcal{P}[\text{reversed path}]} = \frac{P_{\text{eq}}(a_n)}{P_{\text{eq}}(a_0)} = e^{-\beta[V(a_n) - V(a_0)]}, \quad (40)$$

for coordinate-even variables. With inertia, the reversed path also has reversed momenta. This is the pathwise form of microscopic reversibility. It is important to note that $J_{\text{div}} = 0$ does not imply detailed balance $J_i = 0$. A nonequilibrium steady state can have

$$\partial_t P_{\text{ss}} = 0, \quad \nabla \cdot \mathbf{J}_{\text{ss}} = 0, \quad \mathbf{J}_{\text{ss}} \neq 0. \quad (41)$$

Time-reversal symmetry also constrains equilibrium correlation functions. If A and B have time-reversal parities $\epsilon_A, \epsilon_B = \pm 1$, then

$$\langle B(t)A(0) \rangle_{\text{eq}} = \epsilon_A \epsilon_B \langle A(t)B(0) \rangle_{\text{eq}}. \quad (42)$$

For two time-even observables this gives

$$C_{BA}(t) = C_{AB}(t). \quad (43)$$

2.5 Derivation from a partition function

Suppose a constant field h is applied before the observation begins. The equilibrium distribution in the presence of the field is

$$P_h(\Gamma) = \frac{1}{Z_h} e^{-\beta[H_0(\Gamma) - hA(\Gamma)]}. \quad (44)$$

To first order in h ,

$$Z_h = Z_0 \left[1 + \beta h \langle A \rangle_0 + O(h^2) \right], \quad (45)$$

$$P_h(\Gamma) = P_0(\Gamma) \left[1 + \beta h \delta A(\Gamma) + O(h^2) \right]. \quad (46)$$

Now let the system evolve under the unperturbed dynamics after the field is changed. The first-order change in the average of B is

$$\delta \langle B(t) \rangle = \beta h \langle \delta B(t) \delta A(0) \rangle \quad (47)$$

$$= \beta h C_{BA}(t). \quad (48)$$

But a step field is the time integral of its impulse response. Therefore

$$\delta \langle B(t) \rangle = h \int_{-\infty}^t dt' R_{BA}(t - t'). \quad (49)$$

Equating this with Eq. (48) and differentiating with respect to the switching time gives, for $t > 0$,

$$R_{BA}(t) = -\frac{1}{k_B T} \frac{d}{dt} C_{BA}(t). \quad (50)$$

The sign follows from our convention $H_h = H_0 - hA$. For a single observable $A = B$, define the connected correlation

$$C(t) = \langle \delta A(t) \delta A(0) \rangle. \quad (51)$$

Then

$$R(t) = -\frac{1}{k_B T} \Theta(t) \dot{C}(t). \quad (52)$$

This is the classical time-domain fluctuation–dissipation theorem.

3 From fluctuation–dissipation to field correlations

The fluctuation–dissipation theorem that we have just derived is a dynamical statement: it relates a response function to a spontaneous correlation function. There is a closely related static statement that we will need later. Once a coarse-grained field is described by an equilibrium quadratic Hamiltonian, its correlations are obtained by inverting the quadratic kernel. The calculation below follows the Gaussian-functional-integral construction. The important point is that the same object that determines the energetic cost of a fluctuation also determines its correlation function and its response.

3.1 Warm-up: one Gaussian variable

Consider first a single real variable x with Hamiltonian

$$H(x) = \frac{a}{2}x^2 - hx, \quad a > 0. \quad (53)$$

The partition function is

$$Z(h) = \int_{-\infty}^{\infty} dx \exp \left[-\beta \left(\frac{a}{2}x^2 - hx \right) \right]. \quad (54)$$

Complete the square:

$$\frac{a}{2}x^2 - hx = \frac{a}{2} \left(x - \frac{h}{a} \right)^2 - \frac{h^2}{2a}. \quad (55)$$

Therefore

$$Z(h) = Z(0) \exp \left(\frac{\beta h^2}{2a} \right), \quad Z(0) = \sqrt{\frac{2\pi}{\beta a}}. \quad (56)$$

The mean follows from differentiation with respect to the source:

$$\langle x \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial h} = \frac{h}{a}. \quad (57)$$

Hence the static susceptibility is

$$\chi = \frac{\partial \langle x \rangle}{\partial h} = \frac{1}{a}. \quad (58)$$

The connected fluctuation is

$$\langle x^2 \rangle_c = \langle (x - \langle x \rangle)^2 \rangle = \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial h^2} = \frac{1}{\beta a}. \quad (59)$$

Thus

$$\langle x^2 \rangle_c = k_B T \chi. \quad (60)$$

This is the static fluctuation–dissipation relation in its simplest form. We now repeat the calculation for many coupled variables, and then for a field.

3.2 Many coupled Gaussian variables

Let $\phi = (\phi_1, \dots, \phi_N)$ and consider

$$H[\phi] = \frac{1}{2} \sum_{ij} \phi_i A_{ij} \phi_j - \sum_i h_i \phi_i, \quad (61)$$

where A is symmetric and positive definite. In matrix notation,

$$H = \frac{1}{2} \phi^T A \phi - \mathbf{h}^T \phi. \quad (62)$$

Complete the square:

$$H = \frac{1}{2} (\phi - A^{-1} \mathbf{h})^T A (\phi - A^{-1} \mathbf{h}) - \frac{1}{2} \mathbf{h}^T A^{-1} \mathbf{h}. \quad (63)$$

The partition function therefore takes the form

$$Z[\mathbf{h}] = Z[0] \exp\left(\frac{\beta}{2} \mathbf{h}^T A^{-1} \mathbf{h}\right). \quad (64)$$

Differentiating the generating function gives

$$\langle \phi_i \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial h_i} = \sum_j (A^{-1})_{ij} h_j. \quad (65)$$

Therefore the linear susceptibility matrix is

$$\chi_{ij} = \frac{\partial \langle \phi_i \rangle}{\partial h_j} = (A^{-1})_{ij}. \quad (66)$$

A second derivative gives the connected correlation function:

$$\langle \phi_i \phi_j \rangle_c = \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial h_i \partial h_j} = \frac{1}{\beta} (A^{-1})_{ij}. \quad (67)$$

Hence

$$G_{ij} \equiv \langle \phi_i \phi_j \rangle_c = k_B T (A^{-1})_{ij} = k_B T \chi_{ij}. \quad (68)$$

The correlation function is therefore a Green's function: it is the inverse of the operator that appears in the quadratic Hamiltonian.

3.3 Continuum field and functional integral

Replace the discrete label i by the continuous coordinate $\mathbf{r}$, and write a real scalar field $\phi(\mathbf{r})$. The continuum analogue is

$$H[\phi] = \frac{1}{2} \int d^d r d^d r' \phi(\mathbf{r}) \Gamma(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') - \int d^d r h(\mathbf{r}) \phi(\mathbf{r}). \quad (69)$$

The partition function is

$$Z[h] = \int \mathcal{D}\phi \exp[-\beta H[\phi]]. \quad (70)$$

Define the inverse kernel by

$$\int d^d r'' \Gamma(\mathbf{r}, \mathbf{r}'') \Gamma^{-1}(\mathbf{r}'', \mathbf{r}') = \delta^{(d)}(\mathbf{r} - \mathbf{r}'). \quad (71)$$

Complete the square exactly as in the finite-dimensional case:

$$H[\phi] = \frac{1}{2} \int d^d r d^d r' \left[\phi(\mathbf{r}) - \int d^d s \Gamma^{-1}(\mathbf{r}, \mathbf{s}) h(\mathbf{s}) \right] \Gamma(\mathbf{r}, \mathbf{r}') \quad (72)$$

$$\times \left[\phi(\mathbf{r}') - \int d^d s' \Gamma^{-1}(\mathbf{r}', \mathbf{s}') h(\mathbf{s}') \right] \quad (73)$$

$$- \frac{1}{2} \int d^d r d^d r' h(\mathbf{r}) \Gamma^{-1}(\mathbf{r}, \mathbf{r}') h(\mathbf{r}'). \quad (74)$$

The shifted functional integral is independent of h , so

$$Z[h] = Z[0] \exp \left[\frac{\beta}{2} \int d^d r d^d r' h(\mathbf{r}) \Gamma^{-1}(\mathbf{r}, \mathbf{r}') h(\mathbf{r}') \right]. \quad (75)$$

Now differentiate functionally. Since

$$\langle \phi(\mathbf{r}) \rangle = \frac{1}{\beta} \frac{\delta \ln Z}{\delta h(\mathbf{r})}, \quad (76)$$

we obtain

$$\langle \phi(\mathbf{r}) \rangle = \int d^d r' \Gamma^{-1}(\mathbf{r}, \mathbf{r}') h(\mathbf{r}'). \quad (77)$$

Therefore

$$\chi(\mathbf{r}, \mathbf{r}') = \frac{\delta \langle \phi(\mathbf{r}) \rangle}{\delta h(\mathbf{r}')} = \Gamma^{-1}(\mathbf{r}, \mathbf{r}'). \quad (78)$$

A second derivative gives

$$G_c(\mathbf{r}, \mathbf{r}') \equiv \langle \delta \phi(\mathbf{r}) \delta \phi(\mathbf{r}') \rangle \quad (79)$$

$$= \frac{1}{\beta^2} \frac{\delta^2 \ln Z}{\delta h(\mathbf{r}) \delta h(\mathbf{r}')} \quad (80)$$

$$= \frac{1}{\beta} \Gamma^{-1}(\mathbf{r}, \mathbf{r}'). \quad (81)$$

Thus

$$G_c(\mathbf{r}, \mathbf{r}') = k_B T \chi(\mathbf{r}, \mathbf{r}'). \quad (82)$$

This is the field-theoretic form of the static fluctuation–dissipation relation.