Non-Equilibrium Statistical Mechanics

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Chapter 1

Derivation of the Langevin Equation

In this chapter we derive the Langevin equation from a simple mechanical model for a small system (that we will refer to as the Brownian particle) that is in contact with a thermal reservoir which is at thermodynamic equilibrium at time $t = 0$. The full Brownian particle plus thermal reservoir dynamics is assumed to be Hamiltonian. The derivation proceeds in three steps. First, we derive a closed stochastic integrodifferential equation for the dynamics of the Brownian particle, the *G*eneralized Langevin Equation (GLE) . In the second step, we approximate the GLE by a finite dimensional Markovian equation in an extended phase space. Finally, we use singular perturbation theory for Markov processes to derive the Langevin equation, under the assumption of rapidly decorrelating noise. This derivation provides a partial justification for the use of stochastic differential equations, in particular, the Langevin equation, in the modeling of physical systems.

In Section 1.1 we study a simple model for open classical systems and we derive the Generalized Langevin Equation. The Markovian approximation of the GLE is studied in Section 1.2. The derivation of the Langevin equation from this Markovian approximation is studied in Section 1.3. Discussion and bibliographical remarks are included in Section 1.4. Exercises can be found in Section 1.5.

1.1 Open Classical Systems

We consider a particle in one dimension that is in contact with a *t*hermal reservoir (heat bath), a system with infinite heat capacity at temperature β^{-1} that interacts

(exchanges energy) with the particle. We will model the reservoir as a system of infinitely many non-interacting particles which is in thermodynamic equilibrium at time $t = 0$. In other words, we will model the heat bath as a system of infinitely many harmonic oscillators whose initial energy is distributed according to the canonical (Boltzmann-Gibbs) distribution at temperature β^{-1}.

A finite collection of harmonic oscillators is a Hamiltonian system with Hamiltonian

$$H(\mathbf{p}, \mathbf{q}) = \frac{1}{2}\sum_{j=1}^{N} p_j^2 + \frac{1}{2}\sum_{j=1}^{N} q_j^2, \tag{1.1}$$

where for simplicity we have set all the spring constants $\{k_j\}_{j=1}^N$ equal to 1. The corresponding canonical distribution is

$$\mu_\beta(d\mathbf{p}, d\mathbf{q}) = \frac{1}{Z} e^{-\beta H(\mathbf{p},\mathbf{q})}\, dpdq. \tag{1.2}$$

Since the Hamiltonian (1.1) is quadratic in both positions and momenta, the measure (1.2) is Gaussian. We set $\mathbf{z} = (\mathbf{q},\, \mathbf{p}) \in \mathbb{R}^{2N} =: H$ and denote by $\langle \cdot, \cdot \rangle$ the Euclidean inner product in (the Hilbert space) H. Then, for arbitrary vectors $\mathbf{h},\, \mathbf{b} \in H$ we have

$$\mathbb{E}\langle \mathbf{z}, \mathbf{h}\rangle = 0, \quad \mathbb{E}\Big(\langle \mathbf{z}, \mathbf{h}\rangle \langle \mathbf{z}, \mathbf{b}\rangle\Big) = \beta^{-1}\langle \mathbf{h}, \mathbf{b}\rangle. \tag{1.3}$$

We want to consider an infinite dimensional extension of the above model for the heat bath. A natural infinite dimensional extension of a finite system of harmonic oscillators is the wave equation $\partial_t^2\varphi = \partial_x^2\varphi$ that we write as a system of equations

$$\partial_t \varphi = \pi, \quad \partial_t \pi = \partial_x^2 \varphi. \tag{1.4}$$

The wave equation is an infinite dimensional Hamiltonian system with Hamiltonian

$$\mathcal{H}(\pi, \varphi) = \frac{1}{2}\int_{\mathbb{R}} \Big(|\pi|^2 + |\partial_x \varphi|^2\Big)\, dx. \tag{1.5}$$

It is convenient to introduce the Hilbert space H_E with the (energy) norm

$$\|\phi\|^2 = \int_{\mathbb{R}} \Big(|\pi|^2 + |\partial_x \varphi|^2\Big)\, dx \tag{1.6}$$

where $\phi = (\varphi,\, \pi)$. The corresponding inner product is

$$\langle \phi_1, \phi_2\rangle = \int_{\mathbb{R}} \big(\partial_x\varphi_1(x)\overline{\partial_x\varphi_2}(x) + \pi_1(x)\overline{\pi_2}(x)\big)\, dx \tag{1.7}$$

where the overbar denotes the complex conjugate. Using the notation (1.6) we can write the Hamiltonian for the wave equation as

$$\mathcal{H}(\phi) = \frac{1}{2}\|\phi\|^2.$$

We would like to extend the Gibbs distribution (1.2) to this infinite dimensional system. However, the expression

$$\mu_\beta(d\pi d\varphi) = \frac{1}{Z} e^{-\beta \mathcal{H}(\varphi,\pi)} \Pi_{x\in\mathbb{R}}\, d\pi d\varphi \tag{1.8}$$

is merely formal, since Lebesgue measure does not exist in infinite dimensions. However, this measure is Gaussian (the Hamiltonian $\mathcal{H}$ is a quadratic functional in π and ϕ) and the theory of Gaussian measures in Hilbert spaces is well developed. This theory goes beyond the scope of this book[1] For our purposes it is sufficient to note that if X is a Gaussian random variable in the Hilbert space H_E with inner product (1.7) then $\langle X, f\rangle$ is a scalar Gaussian random variable with mean and variance

$$\langle X, f\rangle = 0, \quad \text{and} \quad \mathbb{E}\Big(\langle X, f\rangle\langle X, h\rangle\Big) = \beta^{-1}\langle f, h\rangle. \tag{1.9}$$

Notice the similarity between the formulas in (1.3) and (1.9).

We assume that the full dynamics of the particle coupled to the heat bath is Hamiltonian described by a Hamiltonian function

$$\mathcal{H}(p, q, \pi, \varphi) = H(p, q) + \mathcal{H}_{HB}(\pi, \varphi) + H_I(q, \varphi). \tag{1.10}$$

We use $\mathcal{H}_{HB}(\pi, \phi)$ to denote the Hamiltonian for the wave equation (1.5). $H(p, q)$ denotes the Hamiltonian of the particle, whereas H_I describes the interaction between the particle and the field ϕ. We assume that the coupling is only through the position q and ϕ, it does not depend on the momentum p and the momentum field π. We assume that the particle is moving in a confining potential $V(q)$. Consequently:

$$H(p, q) = \frac{p^2}{2} + V(q). \tag{1.11}$$

Concerning the coupling, we assume that it is linear in the field ϕ and that it is translation invariant:

$$H_I(q, \varphi) = \int_{\mathbb{R}} \varphi(x)\rho(x - q)\, dx. \tag{1.12}$$

[1] Some discussion about Gaussian measures in Hilbert spaces can be found in Section **??**.

The coupling between the particle and the heat bath depends crucially on the function $\rho(x)$ which is arbitrary at this point.[2]

Now we make an approximation that will simplify considerably the analysis: since the particle moves in a confining potential (think of a quadratic potential), we can assume that its position does not change too much. Consequently, we can perform a Taylor series expansion in (1.12) which, together with an integration by parts gives (see Exercise 1)[3]

$$H_I(q,\varphi) \approx q \int_{\mathbb{R}} \partial_x\varphi(x)\rho(x)\,dx. \tag{1.13}$$

The coupling now is linear in both q and φ. This will enable us to integrate out explicitly the fields φ and π from the equations of motion and to obtain a closed equation for the dynamics of the particle.

Putting (1.11), (1.5) and (1.13) together, the Hamiltonian (1.10) becomes

$$\mathcal{H}(p,q,\pi,\phi) = \frac{p^2}{2} + V(q) + \frac{1}{2}\int_{\mathbb{R}} \left(|\pi|^2 + |\partial_x\varphi|^2\right) dx + q\int_{\mathbb{R}} \partial_x\varphi(x)\rho(x)\,dx. \tag{1.14}$$

Now we can derive Hamilton's equations of motion for the coupled particle-field model (1.14):

$$\dot{q} = \frac{\partial\mathcal{H}}{\partial p}, \quad \dot{p} = -\frac{\partial\mathcal{H}}{\partial q}, \tag{1.15a}$$

$$\partial_t\varphi = \frac{\delta\mathcal{H}}{\delta\pi}, \quad \partial_t\pi = -\frac{\delta\mathcal{H}}{\delta\varphi}, \tag{1.15b}$$

where $\frac{\delta\mathcal{H}}{\delta\cdot}$ stands for the functional derivative.[4] Carrying out the differentiations we obtain

$$\dot{q} = p, \quad \dot{p} = -V'(q) - \int_{\mathbb{R}} \partial_x\varphi(x)\rho(x)\,dx, \tag{1.16a}$$

$$\partial_t\varphi = \pi, \quad \partial_t\pi = \partial_x^2\varphi + q\partial_x\rho. \tag{1.16b}$$

Our goal now is to solve equations (1.16b), which is a system of linear inhomogeneous differential equations and then substitute into (1.16a). We will use the

[2] In the terminology of electrodynamics, ρ plays the role of a charge density.

[3] Again, in the terminology of electrodynamics this is called the *dipole approximation* .

[4] We remind the reader that for a functional of the form $\mathcal{H}(\phi) = \int_{\mathbb{R}} H(\phi, \partial_x\phi)\,dx$ the functional derivative is given by $\frac{\delta\mathcal{H}}{\delta\phi} = \frac{\partial H}{\partial\phi} - \frac{\partial}{\partial x}\frac{\partial H}{\partial(\partial_x\rho)}$. We apply this definition to the functional (1.14) to obtain $\frac{\delta\mathcal{H}}{\delta\pi} = \pi, \quad \frac{\delta\mathcal{H}}{\delta\varphi} = -\partial_x^2\varphi - q\partial_x\rho$.

variation of constants formula (*Duhamel's principle*). It is more convenient to rewrite (1.16) in a slightly different form. First, we introduce the operator

$$\mathcal{A} = \begin{pmatrix} 0 & 1 \\ \partial_x^2 & 0 \end{pmatrix}, \tag{1.17}$$

acting on functions in H_E with inner product (1.7). It is not hard to show that the $\mathcal{A}$ is an antisymmetric operator in this space (see Exercise 2). Furthermore, we introduce the notation $\alpha = (\alpha_1(x),\, 0) \in H_E$ with $\partial_x \alpha_1(x) = \rho(x)$. Noticing that

$$\mathcal{A}\alpha = (0,\, \partial_x \rho),$$

we can rewrite (1.16b) in the form

$$\partial_t \phi = \mathcal{A}(\phi + q\alpha) \tag{1.18}$$

with $\phi = (\varphi, \pi)$. Furthermore, the second equation in (1.16) becomes

$$\dot{p} = -V'(q) - \langle \phi, \alpha \rangle. \tag{1.19}$$

Finally, we introduce the function $\psi = \phi + q\alpha$ to rewrite

$$\partial_t \psi = \mathcal{A}\psi + p\alpha. \tag{1.20}$$

Similarly, we introduce ψ in (1.19) to obtain

$$\dot{p} = -V'_{eff}(q) - \langle \psi, \alpha \rangle, \tag{1.21}$$

where

$$V_{eff}(q) = V(q) - \frac{1}{2}\|\alpha\|^2 q^2. \tag{1.22}$$

Notice that

$$\|\alpha\|^2 = \|\rho\|^2_{L^2} =: \lambda.$$

The parameter λ measures the strength of the coupling between the particle and the heat bath. The correction term in the potential $V_{eff}(q)$ is essentially due to the way we have chosen to write the equations of motion for the particle-field system and it is not fundamental; see Exercise 1.

The solution of (1.20) is

$$\psi(t) = e^{\mathcal{A}t}\psi(0) + \int_0^t e^{\mathcal{A}(t-s)} p(s)\alpha \, ds.$$

We substitute this in (1.21) to obtain

$$\begin{aligned}\dot{p} &= -V'_{eff}(q) - \langle \psi, \alpha \rangle \\ &= -V'_{eff}(q) - \left\langle e^{\mathcal{A}t}\psi(0), \alpha \right\rangle - \int_0^t \left\langle e^{\mathcal{A}(t-s)}\alpha, \alpha \right\rangle p(s)\, ds \\ &= -V'_{eff}(q) - \int_0^t \gamma(t-s)p(s)\, ds + F(t)\end{aligned}$$

where

$$F(t) = \left\langle \psi(0), e^{-\mathcal{A}t}\alpha \right\rangle \tag{1.23}$$

and

$$\gamma(t) = \left\langle e^{-\mathcal{A}t}\alpha, \alpha \right\rangle \tag{1.24}$$

Notice that $\psi(0) = \phi(0) + q(0)\alpha$ is a Gaussian field with mean and covariance, using (1.9),

$$\mathbb{E}\langle \psi(0), f \rangle = q(0)\langle \alpha, f \rangle =: \mu_f$$

and

$$\mathbb{E}\left((\langle \psi(0), f \rangle - \mu_f)\left(\langle \psi(0), h \rangle - \mu_h \right) \right) = \beta^{-1}\langle f, h \rangle.$$

To simplify things we will set $q(0) = 0$. Then $F(t)$ is a mean zero stationary Gaussian process with autocorrelation function

$$\begin{aligned}\mathbb{E}(F(t)F(s)) &= \mathbb{E}\left(\left\langle \psi(0), e^{-\mathcal{A}t}\alpha \right\rangle \left\langle \psi(0), e^{-\mathcal{A}s}\alpha \right\rangle \right) \\ &= \beta^{-1}\left\langle e^{-\mathcal{A}t}\alpha, e^{-\mathcal{A}s}\alpha \right\rangle \\ &= \beta^{-1}\gamma(t-s),\end{aligned}$$

where we have used (1.9). Consequently, the autocorrelation function of the stochastic forcing in (1.23) is precisely the kernel (times the temperature) of the dissipation term in the equation for p. This is an example of the *fluctuation-dissipation theorem* .

To summarize, we have obtained a closed equation for the dynamics of the particle, the *G*eneralized Langevin Equation

$$\ddot{q} = -V'_{eff}(q) - \int_0^t \gamma(t-s)\dot{q}(s)\, ds + F(t), \tag{1.25}$$

with $F(t)$ being a mean zero stationary Gaussian processes with autocorrelation function given by the fluctuation–dissipation theorem

$$\mathbb{E}(F(t)F(s)) = \beta^{-1}\gamma(t-s). \tag{1.26}$$

It is clear from formula (1.24) and the definition of α that the autocorrelation function $\gamma(t)$ depends only on the density ρ.[5] In fact, we can show that (see Exercise 3) that

$$\gamma(t) = \int_{\mathbb{R}} |\hat{\rho}(k)|^2 e^{ikt} dk, \tag{1.27}$$

where $\hat{\rho}(k)$ denotes the Fourier transform of ρ.

Let us now make several remarks on the Generelized Langevin Equation (1.25) (GLE). First, notice that the GLE is Newton's equation of motion for the particle, augmented with two additional terms: a linear dissipation term which depends on the history of the particle position and a stochastic forcing term which is related to the the dissipation term through the fluctuation–dissipation theorem (1.26). The fact that the fluctuations (noise) and the dissipation in the systems satisfy such a relation is not surprising, since they have the same source, namely the interaction between the particle and the field. Is is important to note that the noise (and also the fact that it is Gaussian and stationary) in the GLE is due to our assumption that the heat bath is at equilibirum at time $t = 0$, i.e. that the initial equations of the wave equation are distributed according to the (Gaussian) Gibbs measure (1.8). Perhaps surprisingly, the derivation of the GLE and the fluctuation dissipation theorem are not related to our assumption that the heat bath is described by a field, i.e. it is a dynamical system with infinitely many degrees of freedom. We could have arrived at the GLE and the fluctuation–dissipation theorem even if we had only one oscillator in the "heat bath". See Exercise 6.

Furthermore, the autocorrelation function of the noise depends only on the coupling function $\rho(x)$: different choices of the coupling function lead to different noise processes $F(t)$. [6]

It is also important to emphasize the fact that the GLE (1.25) is *equivalent* to the original Hamiltonian dynamics (1.14) with random initial conditions distributed according to (1.8). So far, no approximation has been made. We have merely used the linearity of the dynamics of the heat bath and the linearity of the coupling in order to integrate out the heat bath variables by using the variation of constants formula.

Finally we remark that an alternative way for writing the GLE is

$$\ddot{q} = -V'(q) - \int_0^t D(t-s)q(s)\, ds + F(t) \tag{1.28}$$

[5] Assuming, of course, that the heat bath is described by a wave equation, i.e. assuming that $\mathcal{A}$ is the wave operator.

[6] In fact, the autocorrelation function depends also on the operator A in (1.17).

with

$$D(t) = \langle \mathcal{A} e^{\mathcal{A}t} \alpha, \alpha \rangle. \tag{1.29}$$

The fluctuation-dissipation theorem takes the form

$$\dot{\gamma}(t) = D(t). \tag{1.30}$$

See Exercise 7. When writing the GLE in the form (1.28) there is no need to introduce an effective potential or to assume that $q(0) = 0$.

1.2 The Markovian Approximation

From now on we will ignore the correction in the potential (1.22). We rewrite the GLE (1.25):

$$\ddot{q} = -V'(q) - \int_0^t \gamma(t-s)\dot{q}(s)\, ds + F(t), \tag{1.31}$$

together with the fluctuation-dissipation theorem (1.26). Equation (1.31) is a non-Markovian stochastic equation, since the solution at time t depends on the entire past. In this section we show that when autocorrelation function $\gamma(t)$ decays sufficiently fast, then the dynamics of the particle can be described by a Markovian system of stochastic differential equations in an extended phase space. The basic observation that was already made in Chapter **??**, Exercise **??** that a one dimensional mean zero Gaussian stationary with continuous paths and an exponential autocorrelation function is necessarily the Ornstein-Uhlenbeck process. This is the content of Doob's theorem . Consequently, if the memory kernel (autocorrelation function) $\gamma(t)$ is decaying exponentially fast, then we expect that we can describe the noise in the GLE by adding a finite number of auxiliary variables. We can formalize this by introducing the concept of a *q*uasi-Markovian process quasi-Markovian process:

Definition 1.1. *We will say that a stochastic process X_t is quasi-Markovian if it can be represented as a Markovian stochastic process by adding a finite number of additional variables: there exists a finite dimensional stochastic process Y_t so that $\{X_t, Y_t\}$ is a Markov process.*

In the following result we will use the notation $\langle \cdot, \cdot \rangle$ to denote the Euclidean inner product.

Proposition 1.2. *Let $\lambda \in \mathbb{R}^d$, $A \in \mathbb{R}^{d\times d}$, positive definite, and assume that the autocorrelation function $\gamma(t)$ is given by*

$$\gamma(t) = \langle e^{-At}\lambda, \lambda\rangle. \tag{1.32}$$

Then the GLE (1.31) *is equivalent to the SDE*

$$\begin{aligned}
\dot{q}(t) &= p(t), && \text{(1.33a)}\\
\dot{p}(t) &= -V'(q(t)) + \langle \lambda, z(t)\rangle, && \text{(1.33b)}\\
\dot{z}(t) &= -p(t)\lambda - A\, z(t) + \Sigma\dot{W}(t), \quad z(0) \sim \mathcal{N}(0, \beta^{-1}I), && \text{(1.33c)}
\end{aligned}$$

where $z : \mathbb{R}^+ \mapsto \mathbb{R}^m$, $\lambda \in \mathbb{R}^m$, $\Sigma \in \mathbb{R}^{m\times m}$ and the matrix Σ satisfies

$$\Sigma\Sigma^T = \beta^{-1}(A + A^T). \tag{1.34}$$

Remark 1.3. *Notice that the formula for the autocorrelation function* (1.32) *is similar to* (1.24)*. However, the operator $\mathcal{A}$ in* (1.24) *is the wave operator* (1.17)*, i.e. the generator of a unitary group, whereas the operator A (or, rather, $-A$) that appears in* (1.32) *is the generator of the contraction semigroup e^{-At}, i.e. a dissipative operator. The source of the noise in* (1.25) *and in* (1.33) *is quite different, even though the have the same effect, when the autocorrelation function is exponentially decaying.*

Proof. The solution of (1.33c) is

$$z(t) = e^{-At}z(0) + \int_0^t e^{-A(t-s)}\Sigma dW(s) - \int_0^t e^{-A(t-s)}\lambda p(s)\, ds. \tag{1.35}$$

We substitute this into (1.33b) to obtain

$$\dot{p} = -V'(q) - \int_0^t \gamma(t-s)p(s)\, ds + F(t)$$

with

$$\gamma(t) = \langle e^{-At}\lambda, \lambda\rangle$$

and

$$\begin{aligned}
F(t) &= \left\langle \lambda, e^{-At}z(0) + \int_0^t e^{-A(t-s)}\Sigma dW(s)\right\rangle\\
&=: \langle \lambda, y(t)\rangle\,,
\end{aligned}$$

where

$$y(t) = S(t)z(0) + \int_0^t S(t-s)\Sigma dW(s)$$

with $S(t) = e^{-At}$. With our assumptions on $Z(0)$ and (1.34), $y(t)$ is a mean zero stationary Gaussian process with covariance matrix

$$Q(t-s) = \mathbb{E}(y^T(t)y(s)) = \beta^{-1}S(|t-s|). \tag{1.36}$$

To see this we first note that (using the summation convention)

$$\begin{aligned}\mathbb{E}(y_i(t)y_j(s)) &= S_{i\ell}(t)S_{j\rho}(t)\mathbb{E}(z_\ell(0)z_\rho(0)) + \int_0^t\int_0^s S_{i\rho}(t-\ell)\Sigma_{\rho k}S_{jn}(s-\tau)\Sigma_{nk}\delta(\ell-\tau)\,d\ell dm \\ &= \beta^{-1}S_{i\rho}(t)S_{j\rho}(s) + \int_0^{\min(t,s)} S_{i\rho}(t-\tau)\Sigma_{\rho k}\Sigma_{nk}S_{jn}(s-\tau)\,d\tau.\end{aligned}$$

Consequently, and using (1.34),

$$\begin{aligned}\mathbb{E}(y^T(t)y(s)) &= \beta^{-1}S(t)S^T(s) + \int_0^{\min(t,s)} S(t-\tau)\Sigma^T\Sigma S^T(s-\tau)\,d\tau \\ &= \beta^{-1}S(t)\left(I + \int_0^{\min(t,s)} S(-\tau)(A+A^T)S^T(-\tau)\,d\tau\right)S^T(s).\end{aligned}$$

Without loss of generality we may assume that $s \leqslant t$. Now we claim that

$$\left(I + \int_0^{\min(t,s)} S(-\tau)(A+A^T)S^T(-\tau)\,d\tau\right)S^T(s) = S(-s).$$

To see this, notice that this equation is equivalent to

$$I + \int_0^{t,s} S(-\tau)(A+A^T)S^T(-\tau)\,d\tau = S(s)S^T(-s).$$

This equation is clearly valid at $s = 0$. We differentiate to obtain the identity

$$S(-s)(A+A^T)S^T(-s) = \frac{d}{dt}S(s)S^T(-s),$$

which is true for all s. This completes the proof of (1.36). Now we calculate, with $s \leqslant t$,

$$\begin{aligned}\mathbb{E}(F(t)F(s)) &= \mathbb{E}\left(\langle\lambda, y(t)\rangle\langle\lambda, y(s)\rangle\right) \\ &= \langle Q(t-s)\lambda,\lambda\rangle = \beta^{-1}\langle e^{-At}\lambda,\lambda\rangle \\ &= \beta^{-1}\gamma(t-s)\end{aligned}$$

and the proposition is proved. □ □

Example 1.4. *Consider the case $m = 1$. In this case the vector λ and the matrix A become scalar quantities. The SDE* (1.33) *becomes*

$$\begin{aligned}\dot{q}(t) &= p(t),\\ \dot{p}(t) &= -V'(q(t)) + \lambda z(t),\\ \dot{z}(t) &= -\lambda p(t) - \alpha z(t) + \sqrt{2\alpha\beta^{-1}}\dot{W}(t), \quad z(0) \sim \mathcal{N}(0, \beta^{-1}).\end{aligned}$$

The autocorrelation function is

$$\gamma(t) = \lambda^2 e^{-\alpha t}.$$

Example 1.5. *Consider now the case*

$$\mathcal{A} = \begin{pmatrix} 0 & 1 \\ 1 & -\gamma \end{pmatrix}.$$

The Markovian GLE takes the form

$$\dot{q} = p, \tag{1.37a}$$
$$\dot{p} = -V'(q) + \langle \lambda, \mathbf{z} \rangle, \tag{1.37b}$$
$$\dot{z}_1 = (z_2 + \lambda_1 p), \tag{1.37c}$$
$$\dot{z}_2 = (-z_1 - \gamma z_2 - \lambda_2 p) + \sqrt{2\beta^{-1}\alpha_2}\,\dot{W}. \tag{1.37d}$$

The generator of the dynamics (1.33) is

$$\mathcal{L} = p\partial_q - \partial_q V \partial_p + \langle \lambda, z \rangle \partial_p - p\lambda \cdot \nabla_z - Az \cdot \nabla_z + \frac{1}{2}\beta^{-1} A : D_z, \tag{1.38}$$

where $A : D_z$ denotes the Frobenius inner product between A and the Hessian with respect to z, $A : D_z = \sum_{i,j=1}^{d} A_{ij} \frac{\partial^2}{\partial z_i \partial z_j}$.[7] The Fokker-Planck operator is

$$\mathcal{L}^* = -p\partial_q + \partial_q V \partial_p - \langle \lambda, z \rangle \partial_p + p\lambda \cdot \nabla_z + \nabla_z \cdot (Az\,\cdot) + \frac{1}{2}\beta^{-1} A : D_z. \tag{1.39}$$

When the potential $V(q)$ is confining then the process $X(t) := (q(t), p(t), z(t))$ has nice ergodic properties. We recall that the Hamiltonian of the system is $H(p, q) = \frac{1}{2}p^2 + V(q)$.

[7] In fact, the last term in (1.38) should read $\beta^{-1} A_s : D_z$, where $A_s = \frac{1}{2}(A + A^T)$ denotes the symmetric part of A. However since D_z is symmetric we can write it in the form $\frac{1}{2}\beta^{-1} A : D_z$.

Proposition 1.6. *Assume that the potential V in* (1.33) *is confining. Then the process $X(t) := (q(t),\, p(t),\, z(t))$ is ergodic with invariant distribution*

$$\rho_\beta(q,p,\mathbf{z}) = \frac{1}{Z} e^{-\beta\left(H(p,q)+\frac{1}{2}\|\mathbf{z}\|^2\right)}, \quad Z = \left(2\pi\beta^{-1}\right)^{d+1} \int_{\mathbb{R}} e^{-\beta V(q)}\, dq. \quad (1.40)$$

Proof. We only prove that (1.40) is an invariant distribution. The uniqueness is discussed in Section 1.4. We have to check that ρ_β is a solution of the stationary Fokker-Planck equation

$$\mathcal{L}^*\rho_\beta = 0.$$

We have

$$\left(- p\partial_q + \partial_q V \partial_p\right) e^{-\beta H(q,p)} = 0.$$

Furthermore

$$\left(-\langle \lambda, z\rangle \partial_p + p\lambda\cdot\nabla_z\right) e^{-\beta\left(\frac{1}{2}p^2+\frac{1}{2}\|\mathbf{z}\|^2\right)} = 0.$$

Finally

$$\nabla_z \cdot \left(Az + \frac{1}{2}\beta^{-1} A\nabla_z \right) e^{-\frac{1}{2}\beta\|\mathbf{z}\|^2} = 0.$$

The formula for the partition function follows from Gaussian integration. □

Remark 1.7. *Notice that the invariant distribution is independent of the vector λ and the matrix A.*

As in the case of the Langevin dynamics, we can work in the weighted L^2 space $L^2(\mathbb{R}^{2+d};\rho_\beta)$. In this space the generator (1.38) can be naturally decomposed into its symmetric and antisymmetric parts similarly to the generator of the Langevin dynamics that was studied in Chapter **??**. We denote by A_a and A_s the antisymmetric and symmetric parts of the matrix A, respectively.

Proposition 1.8. *The genrator* (1.38) *can be written as*

$$\mathcal{L} = \mathcal{A} + \mathcal{S}, \quad (1.41)$$

where

$$\mathcal{A} = p\partial_q - \partial_q V \partial_p + \langle \lambda, z\rangle \partial_p - \langle A_a z, \nabla_z\rangle$$

and

$$\mathcal{S} = \langle -A_s z, \nabla_z\rangle + \beta^{-1} A_s : D_z.$$

Furthermore, $\mathcal{A}$ and $\mathcal{S}$ are antisymmetric and symmetric operators, respectively, with respect to the $L^2(\mathbb{R}^{2+d};\rho_\beta)$ inner product.

The proof of this proposition is left as an exercise.

1.3 Derivation of the Langevin Equation

Now we are ready to derive the Langevin equation

$$\dot{q} = p, \quad \dot{p} = -V'(q) - \gamma p + \sqrt{2\gamma\beta^{-1}}\dot{W}, \tag{1.42}$$

and to obtain a formula for the friction coefficient γ. We can derive the dynamics (1.42) from the GLE (1.31) in the limit where the correlation time of the noise becomes very small, $\gamma(t) \to \delta(t)$. This corresponds to taking the coupling in the full Hamiltonian dynamics (1.14) to be localized, $\rho(x) \to \delta(x)$.

We focus on the Markovian approximation (1.33) with the family of autocorrelation functions

$$\gamma^\varepsilon(t) = \frac{1}{\varepsilon^2}\langle e^{-\frac{A}{\varepsilon^2}t}\lambda, \lambda\rangle.$$

This corresponds to rescaling λ and A in (1.33) according to $\lambda \mapsto \lambda/\varepsilon$ and $A \mapsto A/\varepsilon^2$. Equations (1.33) become

$$\dot{q}^\varepsilon(t) = p^\varepsilon(t), \tag{1.43a}$$

$$\dot{p}^\varepsilon(t) = -V'(q^\varepsilon(t)) + \frac{1}{\varepsilon}\langle \lambda, z^\varepsilon(t)\rangle, \tag{1.43b}$$

$$\dot{z}^\varepsilon(t) = -\frac{1}{\varepsilon}p^\varepsilon(t)\lambda - \frac{1}{\varepsilon^2}A\, z^\varepsilon(t) + \frac{1}{\varepsilon}\Sigma\dot{W}(t), \quad z^\varepsilon(0) \sim \mathcal{N}(0, \beta^{-1}I), \tag{1.43c}$$

where (1.34) has been used.

Proposition 1.9. *Let* $\left\{q^\varepsilon(t),\, p^\varepsilon(t),\, z^\varepsilon(t)\right\}$ *denote the solution of* (1.43) *and assume that the matrix* A *is invertible. Then* $\left\{q^\varepsilon(t),\, p^\varepsilon(t)\right\}$ *converges weakly to the solution of the Langevin equation* (1.42) *where the friction coefficient is given by the formula*

$$\gamma(t) = \langle \lambda, A^{-1}\lambda\rangle. \tag{1.44}$$

Remark 1.10. *Notice that* (1.44) *is equivalent to*

$$\gamma = \int_0^{+\infty} \gamma(t)\, dt$$

as well as

$$\gamma = \langle \lambda, \phi\rangle, \quad A\phi = \lambda.$$

These formulas are similar to the ones that we obtained in Chapter **??** *for the diffusion coefficient of a Brownian particle in a periodic potential as well as the ones that we will obtain in Chapter 2 in the context of the Green-Kubo formalism.*

Proof. The backward Kolmogorov equation corresponding to (1.43) is

$$\frac{\partial u^\varepsilon}{\partial t} = \frac{1}{\varepsilon^2}\mathcal{L}_0 + \frac{1}{\varepsilon}\mathcal{L}_1 + \mathcal{L}_2 \tag{1.45}$$

with

$$\begin{aligned}
\mathcal{L}_0 &= -\langle Az, \nabla_z\rangle + \beta^{-1} A : D_z, \\
\mathcal{L}_1 &= \langle \lambda, z\rangle \partial_p - p\langle \lambda, \nabla_z\rangle \\
\mathcal{L}_2 &= p\partial_q - \partial_q V \partial_p.
\end{aligned}$$

We look for a solution to (1.45) in the form of a power series expansion in ε:

$$u^\varepsilon = u_0 + \varepsilon u_1 + \varepsilon^2 u_2 + \dots.$$

We substitute this into (1.45) and equate powers of ε to obtain the sequence of equations

$$\begin{aligned}
\mathcal{L}_0 u_0 &= 0, && \text{(1.46a)} \\
-\mathcal{L}_0 u_1 &= \mathcal{L}_1 u_0, && \text{(1.46b)} \\
-\mathcal{L}_0 u_2 &= \mathcal{L}_1 u_1 + \mathcal{L}_2 u_0 - \frac{\partial u_0}{\partial t}. && \text{(1.46c)} \\
\dots &= \dots
\end{aligned}$$

From the first equation we deduce that to leading order the solution of the Kolmogorov equation is independent of the auxiliary variables $\mathbf{z}$, $u_0 = u(q,p,t)$. The solvability of the second equation reads

$$\int_{\mathbb{R}^d} \mathcal{L}_1 u_0 e^{-\frac{\beta}{2}\|\mathbf{z}\|^2}\, dz = 0,$$

which is satisfied, since

$$\mathcal{L}_1 u_0 = \langle \lambda, \mathbf{z}\rangle \frac{\partial u}{\partial t}.$$

The solution to the equation

$$-\mathcal{L}_0 u_1 = \langle \lambda, \mathbf{z}\rangle \frac{\partial u}{\partial t}$$

is

$$u_1(q,p,t) = \langle (A^T)^{-1}\lambda, \mathbf{z}\rangle \frac{\partial u}{\partial t},$$

plus an element in the null space of $\mathcal{L}_0$, which, as we know from similar calculation that we have already done, for example in Section **??** will not affect the limiting equation.

Now we use the solvability condition for (1.46c) to obtain the backward Kolmogorov equation corresponding to the Langevin equation. The solvability condition gives

$$\frac{\partial u}{\partial t} = \mathcal{L}_2 u + \langle \mathcal{L}_1 u_1 \rangle_\beta,$$

where

$$\langle \cdot \rangle_\beta := \left(2\pi\beta^{-1}\right)^{-d} \int_{\mathbb{R}^d} \cdot e^{-\frac{\beta}{2}\|\mathbf{z}\|^2}\, dz.$$

We calculate

$$\langle \mathcal{L}_1 u_1 \rangle_\beta = \beta^{-1} \langle (A^T)^{-1}\lambda, \lambda \rangle \frac{\partial^2 u}{\partial p^2} - \langle (A^T)^{-1}\lambda, \lambda \rangle p \frac{\partial u}{\partial p}.$$

Consequently, u is the solution of the PDE

$$\frac{\partial u}{\partial t} = \left(p\partial_q - \partial_q V \partial_p - \gamma p \partial_p + \beta^{-1}\partial_p^2\right) u,$$

where γ is given by (1.44). This is precisely the backward Kolmogorov equation of the Langevin equation (1.42). □

1.4 Discussion and Bibliography

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Section 1.1 is based on [42]. The Generalized Langevin equation was studied extensively in [19, 20, 21] where existence and uniqueness of solutions as well as ergodic properties were established. An early reference on the construction of heat baths is [32]. The ergodic properties of a chain of anharmonic oscillators, coupled to two Markovian heat baths (i.e. with an exponential autocorrelation function) at different temperatures were studied in [10, 11, 9, 43]. The Markovian approximation of the Generalized Langevin equation was studied in [29]. See also [37].

A natural question that arises is whether it is possible to approximate the GLE equation (1.25) with an arbitrary memory kernel by a Markovian system of the form (1.33). This essentially a problem in approximation theory that was studied in [46, 26, 25]. A systematic methodology for obtaining Markovian approximations to the GLE, which is based on the continued fraction expansion of the Laplace

transform of the autocorrelation function of the noise in the GLE, was introduced by Mori in [36].

Another model for an open classical system that has been studied extensively is based on a finite dimensional heat bath. A calculation similar to the one that we have done in Section 1.1 leads to a GLE in which the noise depends on the number of particles in the heat bath. One then passes to the thermodynamic limit i.e. the limit where the number of particles in the heat bath becomes infinite to obtain the GLE; see Exercise 6. This model is called the *K*ac–Zwanzig model and was introduced in [13, 49]. See also [12]. Further information on the Kac-Zwanzig model can be found in [33, 5, 14, 2]. Nonlinear coupling between the distinguished particle and the harmonic heat bath is studied in [30]. The Kac-Zwanzig model can be used in order to compare between the results of reaction rate theory that was developed in Chapter **??** with techniques for calculating reaction rates that are appropriate for Hamiltonian systems such as *transition state theory*. See [16, 39, 1, 38].

We emphasize the fact that the GLE obtained in sections **??** and **??** from the coupled particle-field model (1.10) is *exact*. Of course, all the information about the environment is contained in the noise process and the autocorrelation function. The rather straightforward derivation of the GLE is based on the linearity of the thermal reservoir and on the linear coupling. Similar derivations are also possible for more general Hamiltonian systems of the form (**??**) using projection operator techniques. This approach is usually referred to as the *Mori-Zwanzig formalism* . This approach is developed in many books on non-equilibrium statistical mechanics [35, 28, 50]. It is possible to derive Langevin (or Fokker-Planck) equations in some appropriate asymptotic limit, for example, in the limit as the ratio between the mass of the particles in the bath and the (much heavier) Brownian particle tends to 0. See [35, 47]. This asymptotic limit goes back to Einstein's original work on Brownian motion. A rigorous study of such a model is presented in [8].

1.5 Exercises

1. Derive (1.13) from (1.12). Show that the next term in the expansion compensates for the correction term in the effective potential (1.22).

2. Show that the operator $\mathcal{A}$ defined in (1.17) is antisymmetric in the Hilbert space H_E with inner product (1.7). Conclude that $(e^{\mathcal{A}t})* = e^{-\mathcal{A}t}$. Prove that the

one parameter family of operators e^{cAt} forms a *u*nitary group (This is usually referred to as *S*tone's theorem . See [40].

3. Solve the wave equation (1.4) by taking the Fourier transform. In particular, calculate $e^{-\mathcal{A}t}$ in Fourier space. Use this to prove (1.27).

4. Solve the GLE (1.31) for the free particle $V \equiv 0$ and when the potential is quadratic (hint: use the Laplace transform, see [29]).

5. (a) Consider a system of N harmonic oscillators governed by the Hamiltonian

$$H(\mathbf{q},\, \mathbf{p}) = \sum_{j=1}^{N} \frac{p_j^2}{2m_j} + \frac{k_j}{2} q_j^2$$

$q,\, p \in \mathbb{R}^N$. Assume that the initial conditions are distributed according to the distribution $\frac{1}{Z} e^{-\beta H(\mathbf{p},\mathbf{q})}$ with $\beta > 0$. Compute the average kinetic energy for this system as a function of time.

(b) Do the same calculation for the Hamiltonian

$$H(\mathbf{q},\, \mathbf{p}) = \frac{1}{2}\langle A\mathbf{p}, \mathbf{p}\rangle + \frac{1}{2}\langle B\mathbf{q}, \mathbf{q}\rangle$$

where $q,\, p \in \mathbb{R}^N$, $A,\, B \in \mathbb{R}^{N\times N}$ are symmetric strictly positive definite matrices and the initial conditions are distributed according to $\frac{1}{Z} e^{-\beta H(\mathbf{p},\mathbf{q})}$.

6. (The Kac-Zwanzig model) . Consider the Hamiltonian

$$H(Q_N, P_N, q, p) = \frac{P_N^2}{2} + V(Q_N) + \sum_{n=1}^{N} \left[\left(\frac{p_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 q_n^2 \right) - \lambda \mu_n q_n Q_N \right] \quad (1.47)$$

where the subscript N in the notation for the position and momentum of the distinguished particle, Q_N and P_N emphasizes their dependence on the number N of the harmonic oscillators in the heat bath, $V(Q)$ denotes the potential experienced by the Brownian particle and $\lambda > 0$ is the coupling constant. Assume that the initial conditions of the Brownian particle are deterministic and that the those of the particles in the heat bath are Gaussian distributed according to the distribution $\frac{1}{Z} e^{-\beta H(\mathbf{p},\,\mathbf{q})}$.

(a) Obtain the Generalized Langevin equation and prove the fluctuation–dissipation theorem.

(b) Assume that the frequencies $\{\omega_n\}_{n=1}^N$ are random variables. Investigate under what assumptions on their distribution it is possible to pass to the thermodynamic limit (see [14]).

7. Derive equations (1.28), (1.29) and (1.30).

8. Prove Proposition 1.8.

9. Analyze the modelds studied in this paper in the multidimensional case, i.e. when the Brownian particle is a d–dimensional Hamiltonian system.

Chapter 2

Linear Response Theory for Diffusion Processes

In this chapter we study the effect of a weak external forcing to a system at equilibrium. The forcing moves the system away from equilibrium and we are interested in understanding the response of the system to this forcing. We study this problem for ergodic diffusion processes using perturbation theory. In particular, we develop *linear response theory*. The analysis of weakly perturbed systems leads to fundamental results such as the *fluctuation-dissipation theorem* and to the Green-Kubo formula that enables us to calculate transport coefficients.

Linear response theory is developed in Section 2.1. The fluctuation-dissipation theorem is presented in Section 2.2. Einstein's relation, The Green-Kubo formula and the fluctuation-dissipation theorem are studied in Section 2.3. Discussion and bibliographical remarks are included in Section 2.4. Exercises can be found in Section 2.5.

2.1 Linear Response Theory

The (somewhat abstract) setting that we will consider in the following. Let X_t denote a stationary dynamical system with state space $\mathbb{X}$ and invariant measure $\mu(dx) = f_\infty(x)\,dx$. We probe the system by adding a time dependent forcing $\varepsilon F(t)$ with $\varepsilon \ll 1$ at time t_0.[1]. Our goal is to calculate the distribution function $f^\varepsilon(x,t)$ of the perturbed systems X_t^ε, $\varepsilon \ll 1$, in particular in the long time limit

[1]The natural choice is $t_0 = 0$ Sometimes it is convenient to take $t_0 = -\infty$.

$t \to +\infty$. We can then calculate the expectation value of observables as well as correlation functions.

We assume that the distribution function $f^\varepsilon(x,t)$ satisfies a linear kinetic equation e.g. the Liouville or the Fokker-Planck equation:[2]

$$\frac{\partial f^\varepsilon}{\partial t} = \mathcal{L}^{*\,\varepsilon} f^\varepsilon, \tag{2.1a}$$

$$f^\varepsilon\big|_{t=t_0} = f_\infty. \tag{2.1b}$$

The choice of the initial conditions reflects the fact that at $t = t_0$ the system is at equilibrium.

The operator $\mathcal{L}^{*\,\varepsilon}$ can be written in the form

$$\mathcal{L}^{*\,\varepsilon} = \mathcal{L}_0^* + \varepsilon \mathcal{L}_1^*, \tag{2.2}$$

where $\mathcal{L}_0^*$ denotes the Liouville or Fokker-Planck operator of the unperturbed system and $\mathcal{L}_1^*$ is related to the external forcing. Throughout this section we will assume that $\mathcal{L}_1$ is of the form

$$\mathcal{L}_1^* = F(t) \cdot D, \tag{2.3}$$

where D is some linear (differential) operator. Since f_∞ is the unique equilibrium distribution, we have that

$$\mathcal{L}_0^* f_\infty = 0. \tag{2.4}$$

Before we process with the analysis of (2.1) we present a few examples.

Example 2.1. (A deterministic dynamical system). *Let X_t be the solution of the differential equation*

$$\frac{dX_t}{dt} = h(X_t), \tag{2.5}$$

on a (possibly compact) state space $\mathbb{X}$. We add a weak time dependent forcing to obtain the dynamics

$$\frac{dX_t}{dt} = h(X_t) + \varepsilon F(t). \tag{2.6}$$

[2]Note that, in order to be consistent with the notation that we have used previously in these notes, in (2.1a) we use $\mathcal{L}^*$ instead of $\mathcal{L}$, since the operator that appears in the Liouville or the Fokker-Planck equation is the adjoint of the generator.

We assume that the unperturbed dynamics has a unique invariant distribution f_∞ which is the solution of the stationary Liouville equation

$$\nabla \cdot \Big(h(x) f_\infty \Big) = 0, \tag{2.7}$$

equipped with appropriate boundary conditions. The operator $\mathcal{L}^{*\,\varepsilon}$ in (2.2) *has the form*

$$\mathcal{L}^{*\,\varepsilon} \cdot = -\nabla \cdot \Big(h(x) \cdot \Big) - \varepsilon F(t) \cdot \nabla \cdot .$$

In this example, the operator D in (2.3) *is $D = -\nabla$.*

A particular case of a deterministic dynamical system of the form (2.5), and the most important in statistical mechanics, is that of an N-body Hamiltonian system.

Example 2.2. (A stochastic dynamical system). *Let X_t be the solution of the stochastic differential equation*

$$dX_t = h(X_t)\, dt + \sigma(X_t)\, dW_t, \tag{2.8}$$

on $\mathbb{R}^d$, where $\sigma(x)$ is a positive semidefinite matrix and where the Itô interpretation is used. We add a weak time dependent forcing to obtain the dynamics

$$dX_t = h(X_t)\, dt + \varepsilon F(t)\, dt + \sigma(X_t)\, dW_t. \tag{2.9}$$

We assume that the unperturbed dynamics has a unique invariant distribution f_∞ which is the solution of the stationary Fokker-Planck equation

$$-\nabla \cdot \Big(h(x) f_\infty \Big) + \frac{1}{2} D^2 : \Big(\Sigma(x) f_\infty \Big) = 0, \tag{2.10}$$

where $\Sigma(x) = \sigma(x)\sigma^T(x)$. The operator $\mathcal{L}^{*\,\varepsilon}$ in (2.2) *has the form*

$$\mathcal{L}^{*\,\varepsilon} \cdot = -\nabla \cdot \Big(h(x) \cdot \Big) + \frac{1}{2} D^2 : \Big(\Sigma(x) \cdot \Big) - \varepsilon F(t) \cdot \nabla \cdot :$$

As in the previous example, the operator D in (2.3) *is $D = -\nabla$.*

Example 2.3. *A particular case of Example 2.2 is the Langevin equation:*

$$\ddot{q} = -\nabla V(q) + \varepsilon F(t) - \gamma \dot{q} + \sqrt{2\gamma\beta}\, \dot{W}. \tag{2.11}$$

Writing (2.13) *as a system of SDEs we have*

$$dq_t = p_t\, dt, \quad dp_t = -\nabla V(q_t)\, dt + \varepsilon F(t)\, dt - \gamma p_t\, dt + \sqrt{2\gamma\beta}\, dW_t. \tag{2.12}$$

For this example we have $D = -\nabla_p$ and, assuming that V is a confining potential, $f_\infty = \frac{1}{Z} e^{-\beta H(p,q)}$, $H(p,q) = \frac{1}{2}p^2 + V(q)$. We will study this example in detail later on.

Example 2.4. *Consider again the Langevin dynamics with a time-dependent temperature. The perturbed dynamics is*

$$dq_t = p_t\,dt, \quad dp_t = -\nabla V(q_t)\,dt - \gamma p_t\,dt + \sqrt{2\gamma\beta^{-1}(1+\varepsilon T(t))}\,dW_t, \tag{2.13}$$

with $1+\varepsilon T(t) > 0$*. In this case the operator* D *is*

$$D = \gamma\beta^{-1}\Delta_p.$$

The general case where both the drift and the diffusion are perturbed is considered in Exercise 1.

Now we proceed with the analysis of (2.1). We look for a solution in the form of a power series expansion in ε:

$$f^\varepsilon = f_0 + \varepsilon f_1 + \dots. \tag{2.14}$$

We substitute this into (2.1a) and use the initial condition (2.1b) to obtain the equations

$$\frac{\partial f_0}{\partial t} = \mathcal{L}_0^* f_0, \quad f_0\big|_{t=0} = f_\infty, \tag{2.15a}$$

$$\frac{\partial f_1}{\partial t} = \mathcal{L}_0^* f_1 + \mathcal{L}_1^* f_0, \quad f_1\big|_{t=0} = 0. \tag{2.15b}$$

The only solution to (2.15a) is

$$f_0 = f_\infty.$$

We use this into (2.15b) and use (2.3) to obtain

$$\frac{\partial f_1}{\partial t} = \mathcal{L}_0^* f_1 + F(t)\cdot Df_\infty, \quad f_1\big|_{t=0} = 0.$$

We use the variation of constants formula to solve this equation:

$$f_1(t) = \int_{t_0}^t e^{\mathcal{L}_0^*(t-s)} F(s)\cdot Df_\infty\,ds. \tag{2.16}$$

It is possible to calculate higher order terms in the expansion for f^ε; see Exercise 2. For our purposes the calculation of $f_1(t)$ is sufficient.

Now we can calculate the deviation in the expectation value of an observable due to the external forcing. Let $\langle\cdot\rangle_{eq}$ and $\langle\cdot\rangle$ denote the expectation value with

respect to f_∞ and f^ε, respectively. Let $A(\cdot)$ be an observable (phase-space function) and denote by $A(t)$ the deviation of its expectation value from equilibrium, to leading order:

$$\begin{aligned} A(t) &:= \langle A(X_t)\rangle - \langle A(X_t)\rangle_{eq} \\ &= \int A(x)\big(f^\varepsilon(x,t) - f_{eq}(x)\big)\,dx \\ &= \varepsilon \int A(x)\left(\int_{t_0}^t e^{\mathcal{L}_0^*(t-s)}F(s)\cdot Df_\infty\,ds\right)dx. \end{aligned}$$

Assuming now that we can interchange the order of integration we can rewrite the above formula as

$$\begin{aligned} A(t) &= \varepsilon \int A(x)\left(\int_{t_0}^t e^{\mathcal{L}_0^*(t-s)}F(s)\cdot Df_\infty\,ds\right)dx \\ &= \varepsilon \int_{t_0}^t \left(\int A(x)e^{\mathcal{L}_0^*(t-s)}\cdot Df_\infty\,dx\right)ds \\ &=: \varepsilon \int_{t_0}^t R_{\mathcal{L}_0,A}(t-s)F(s)\,ds, \end{aligned} \tag{2.17}$$

where we have defined the *response function*

$$R_{\mathcal{L}_0,A}(t) = \int A(x)e^{\mathcal{L}_0^* t}\cdot Df_\infty\,dx \tag{2.18}$$

We set now the lower limit of integration in (2.17) to be $t_0 = -\infty$ (we extend the definition of $R_{\mathcal{L}_0,A}(t)$ in (2.18) to be 0 for $t<0$) and assume that $R_{\mathcal{L}_0,A}(t)$ decays to 0 as $t\to+\infty$ sufficiently fast so that we can extend the upper limit of integration to $+\infty$ to write

$$A(t) = \varepsilon \int_{-\infty}^{+\infty} R_{\mathcal{L}_0,A}(t-s)F(s)\,ds, \tag{2.19}$$

As expected (since we have used linear perturbation theory), the deviation of the expectation value of an observable from its equilibrium value is a linear function of the forcing term. Notice also that (2.19) has the form of the solution of a linear differential equation with $R_{\mathcal{L}_0,A}(t)$ playing the role of the Green's function. If we consider a delta-like forcing at $t=0$, $F(t)=\delta(t)$, then the above formula gives

$$A(t) = \varepsilon R_{\mathcal{L}_0,A}(t).$$

Thus, the response function gives the deviation of the expectation value of an observable from equilibrium for a delta-like force.

Consider now a constant force that is exerted to the system at time $t = 0$, $F(t) = F\Theta(t)$ where $\Theta(t)$ denotes the Heaviside step function. For this forcing (2.17) becomes

$$A(t) = \varepsilon F \int_0^t R_{\mathcal{L}_0,A}(t-s)\,ds. \tag{2.20}$$

Example 2.5 (Stochastic Resonance, see Sec.**??**)**.** *Linear response theory provides us with a very elegant method for calculating the noise amplification factor for a particle moving in a double well potential in the presence of thermal fluctuations under the influence of a weak external forcing. We consider the model (cf. eqn.* (**??**)*)*

$$dX_t = -V'(X_t)\,dt + A_0\cos(\omega_0 t)\,dt + \sqrt{2\beta^{-1}}\,dW. \tag{2.21}$$

Our goal is to calculate the average position $\langle X_t\rangle$ *in the regime* $A_0 \ll 1$*. We can use* (2.17) *and* (2.18)*. The generator of the unperturbed dynamics is the generator of the reversible dynamics*

$$dX_t = -V'(X_t)\,dt + \sqrt{2\beta^{-1}}\,dW_t.$$

We have

$$D = -\frac{\partial}{\partial x}, \quad f_\infty(x) = \frac{1}{Z}e^{-\beta V(x)}, \quad F(t) = \cos(\omega_0 t).$$

The observable that we are interested in is the particle position. The response function is

$$\begin{aligned} R_{\mathcal{L}_0,x}(t) &= \int x e^{\mathcal{L}_0^* t}\left(-\frac{\partial}{\partial x}f_\infty(x)\right)dx \\ &= \beta\int \left(e^{\mathcal{L}_0 t}x\right)V'(x)f_\infty(x)\,dx \\ &= \beta\langle X_t V'(X_t)\rangle_{eq}. \end{aligned}$$

Let now $\{\lambda_\ell,\,\phi_\ell\}_{\ell=0}^\infty$ *denote the eigenvalues and eigenfunctions of the unperturbed generator* (**??**)*. We calculate (see Exercise* **??***)*

$$\langle X_t V'(X_t)\rangle_{eq} = \sum_{\ell=1}^\infty g_\ell e^{-\lambda_\ell t}$$

with

$$g_\ell = \langle x, \phi_\ell \rangle_{f_\infty} \langle V'(x), \phi_\ell \rangle_{f_\infty},$$

with $\langle g, h \rangle_{f_\infty} = \int g(x)h(x)f_\infty(x)\,dx$*. Consequently (remember that* $\langle X_t \rangle_{eq} = 0$*; furthermore, to ensure stationarity, we have set* $t_0 = -\infty$*)*

$$\begin{aligned} \langle X_t \rangle &= \beta A_0 \int_{-\infty}^{t} \sum_{\ell=1}^{\infty} g_\ell e^{-\lambda_\ell (t-s)} \cos(\omega_0 s)\, ds \\ &= \frac{\beta A_0}{2} \sum_{\ell=1}^{\infty} g_\ell Re\left(\frac{e^{i\omega_0 t}}{\lambda_\ell + i\omega_0} \right). \end{aligned}$$

We introduce now the susceptibility

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = \sum_{\ell=1}^{\infty} \frac{g_\ell}{\lambda_\ell + i\omega},$$

to rewrite

$$\langle X_t = \rangle \bar{x} \cos(\omega_0 t - \bar{\phi}) \tag{2.22}$$

with

$$\bar{x} = \beta A_0 |\chi(\omega_0)| \quad \textit{and} \quad \bar{\phi} = \arctan\left(\frac{\chi''(\omega_0)}{\chi''(\omega_0)} \right). \tag{2.23}$$

The noise amplification factor (see eqn.), in the linear response approximation is

$$\eta = \beta |\chi(\omega_0)|^2. \tag{2.24}$$

As expected, it is independent of the amplitude of the oscillations. and it depends only on the spectrum of the generator of the unperturbed dynamics and the temperature.

2.2 The Fluctuation–Dissipation Theorem

In this section we establish a connection between the response function (2.18) and stationary autocorrelation functions. Let X_t be a stationary Markov process in $\mathbb{R}^d$ with generator $\mathcal{L}$ and invariant distribution f_∞ and let $A(\cdot)$ and $B(\cdot)$ be two

observables. The stationary autocorrelation function $\langle A(X_t)B(X_0)\rangle_{eq}$ (see Equation (**??**)) can be calculated as follows

$$\begin{aligned}
\kappa_{A,B}(t) &:= \langle A(X_t)B(X_0)\rangle_{eq} \\
&= \int\int A(x)B(x_0)p(x,t|x_0,0)f_\infty(x_0)\,dxdx_0 \\
&= \int\int A(x)B(x_0)e^{\mathcal{L}^* t}\delta(x-x_0)f_\infty(x_0)\,dxdx_0 \\
&= \int\int e^{\mathcal{L}t}A(x)B(x_0)\delta(x-x_0)f_\infty(x_0)\,dxdx_0 \\
&= \int e^{\mathcal{L}t}A(x)B(x)f_\infty(x)\,dx,
\end{aligned}$$

where $\mathcal{L}$ and $\mathcal{L}^*$ act on functions of x. Thus we have established the formula

$$\kappa_{A,B}(t) = \big(S_t A(x), B(x)\big)_{f_\infty}, \tag{2.25}$$

where $S_t = e^{\mathcal{L}t}$ denotes the semigroup generated by $\mathcal{L}$ and $\big(\cdot,\cdot\big)_{f_\infty}$ denotes the L^2 inner product weighted by the invariant distribution of the diffusion process.

Consider now the particular choice $B(x) = f_\infty^{-1}Df_\infty$. We combine (2.18) and (2.25) to deduce

$$\kappa_{A,f_\infty^{-1}Df_\infty}(t) = R_{\mathcal{L}_0,A}(t). \tag{2.26}$$

This is a version of the *fluctuation-dissipation theorem* and it forms one of the cornerstones of non-equilibrium statistical mechanics. In particular, it enables us to calculate equilibrium correlation functions by measuring the response of the system to a weak external forcing.

Example 2.6. *Consider the Langevin equation from Example 2.3 in one dimension with a constant external forcing:*

$$\ddot{q} = -\partial_q V(q) + \varepsilon F - \gamma\dot{q} + \sqrt{2\gamma\beta}\dot{W}.$$

We have $D = -\partial_p$ *and*

$$B = f_\infty^{-1}Df_\infty = \beta p.$$

We use (2.26) *with* $A = p$*:*

$$R_{\mathcal{L}_0,p}(t) = \beta\langle p(t)p(0)\rangle_{eq}.$$

When the potential is harmonic, $V(q) = \frac{1}{2}\omega_0^2 q^2$, we can compute explicitly the response function and, consequently, the velocity autocorrelation function at equilibrium:[3]

$$R_{\mathcal{L}_0,q}(t) = \frac{1}{\omega_1} e^{-\frac{\gamma t}{2}} \sin(\omega_1 t), \quad \omega_1 = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}$$

and

$$R_{\mathcal{L}_0,p}(t) = e^{-\frac{\gamma t}{2}} \left(\cos(\omega_1 t) - \frac{\gamma}{2\omega_1} \sin(\omega_1 t) \right).$$

Consequently:

$$\langle p(t)p(0)\rangle_{eq} = \beta^{-1} e^{-\frac{\gamma t}{2}} \left(\cos(\omega_1 t) - \frac{\gamma}{2\omega_1} \sin(\omega_1 t) \right).$$

Similar calculations can be done for more general linear SDEs. See Exercise 5.

Example 2.7. *Consider again the Langevin dynamics with a perturbation in the temperature*

$$dq = p\,dt, \quad dp = -V'(q)\,dt + F\,dt - \gamma p\,dt + \sqrt{2\gamma\beta^{-1}(1+F)}\,dW_t.$$

We have $D = \gamma\beta^{-1}\partial_p^2$ and

$$B = f_\infty^{-1} D f_\infty = \gamma\beta(p^2 - \beta^{-1}).$$

Let $H(p,q) = p^2/2 + V(q)$ denote the total energy. We have

$$f_\infty^{-1}\mathcal{L}_0^* H(p,q) f_\infty = \mathcal{L}_0 H(p,q) = \gamma(-p^2 + \beta^{-1}).$$

Consequently (see Exercise 6):

$$\kappa_{A, f_\infty^{-1} D f_\infty}(t) = -\beta \frac{d}{dt} \kappa_{A,H}(t). \tag{2.27}$$

Setting now $A = H$ we obtain

$$R_{H,\mathcal{L}}(t) = -\beta \frac{d}{dt} \langle H(t)H(0)\rangle_{eq}.$$

[3] Notice that this is the Green's function for the damped harmonic oscillator.

2.3 Einstein's Relation and the Green-Kubo Formula

Let us now calculate the long time limit of $A(t)$ when the external forcing is a step function. The following formal calculations can be justified in particular cases, for example for reversible diffusion process in which case the generator of the process is a self-adjoint operator (in the right function space) and functional calculus can be used.

We calculate:

$$\begin{aligned}
\int_0^t R_{\mathcal{L},A}(t-s)\,ds &= \int_0^t \int A(x) e^{\mathcal{L}_0(t-s)} Df_\infty \,dx\,ds \\
&= \int \int_0^t \left(e^{\mathcal{L}(t-s)} A(x) \right) Df_\infty \,ds\,dx \\
&= \int \left(e^{\mathcal{L}_0 t} \int_0^t e^{\mathcal{L}(-s)}\,ds A(x) \right) Df_\infty \,dx \\
&= \int \left(e^{\mathcal{L}_0 t} (-\mathcal{L}_0)^{-1} \left(e^{\mathcal{L}_0(-t)} - I \right) A(x) \right) Df_\infty \,dx \\
&= \int \left(\left(I - e^{\mathcal{L}_0 t} \right) (-\mathcal{L})^{-1} A(x) \right) Df_\infty \,dx
\end{aligned}$$

Assuming now that $\lim_{t\to+\infty} e^{\mathcal{L}t} = 0$ (again, think of reversible diffusions) we have that

$$\Sigma := \lim_{t\to+\infty} \int_0^t R_{\mathcal{L},A}(t-s)\,ds = \int (-\mathcal{L})^{-1} A(x) Df_\infty \,dx. \tag{2.28}$$

Using this in (2.20) and relabeling $\varepsilon F \mapsto F$ we obtain

$$\lim_{F\to 0} \lim_{t\to+\infty} \frac{A(t)}{F} = \int (-\mathcal{L})^{-1} A(x) Df_\infty \,dx. \tag{2.29}$$

Notice that we can interchange the order with which we take the limits in (2.29). We will see later that formulas of the form (2.29) enable us to calculate *transport coefficients*, such as the diffusion coefficient. We remark also that we can rewrite the above formula in the form

$$\lim_{F\to 0} \lim_{t\to+\infty} \frac{A(t)}{F} = \int \phi Df_\infty \,dx,$$

where ϕ is the solution of the Poisson equation

$$-\mathcal{L}\phi = A(x), \tag{2.30}$$

equipped with appropriate boundary conditions. This is precisely the formalism that was used in Chapter **??** in the study of Brownian motion in periodic potentials:

Example 2.8. *Consider the Langevin dynamics in a periodic or random potential.*

$$dq_t = p_t\,dt, \quad dp_t = -\nabla V(q_t)\,dt - \gamma p_t\,dt + \sqrt{2\gamma\beta^{-1}}\,dW.$$

From Einstein's formula (**??**) *we have that the diffusion coefficient is related to the mobility according to*

$$D = \beta^{-1} \lim_{F\to 0} \lim_{t\to+\infty} \frac{\langle p_t\rangle}{F}$$

where we have used $\langle p_t\rangle_{eq} = 0$. *We use now* (2.28) *with* $A(t) = p_t$, $D = -\nabla_p$, $f_\infty = \frac{1}{Z}e^{-\beta H(q,p)}$ *to obtain*

$$D = \int\int \phi p f_\infty\,dpdq = \langle -\mathcal{L}\phi, \phi\rangle_{f_\infty}, \tag{2.31}$$

which is precisely the formula obtained from homogenization theory.

Notice also that, upon combining (2.26) with (2.29) we obtain

$$\Sigma = \lim_{t\to+\infty} \int_0^t \kappa_{A, f_\infty^{-1} D f_\infty}(t-s)\,ds. \tag{2.32}$$

Thus, a transport coefficient can be computed in terms of the time integral of an appropriate autocorrelation function. This is an example of the *Green-Kubo formula* .

We can obtain a more general form of the Green-Kubo formalism as follows. First, we define the generalized drift and diffusion coefficients as follows (compare with (**??**) and (**??**)):

$$V^f(x) = \lim_{h\to 0} \frac{1}{h}\mathbb{E}\Big(f(X_h) - f(X_0)\Big|X_0 = x\Big) = \mathcal{L}f \tag{2.33}$$

and

$$\begin{aligned} D^{f,g}(x) &:= \lim_{h\to 0} \frac{1}{h}\mathbb{E}\Big((f(X_{t+h}) - f(X_t))((g(X_{t+h}) - g(X_t))\Big|X_t = x\Big) \\ &= \mathcal{L}(fg)(x) - (g\mathcal{L}f)(x) - (f\mathcal{L}g)(x), \end{aligned} \tag{2.34}$$

where f, g are smooth functions.[4] The equality in (2.33) follows from the definition of the generator of a diffusion process. For the equality in (2.34) see Exercise 3. Sometimes $D^{f,g}(x)$ is called the *opérateur carré du champ* .

We have the following result.

[4] In fact, all we need is $f,\ g \in D(\mathcal{L})$ and $fg \in D(\mathcal{L})$.

Theorem 2.9. *[The Green-Kubo formula] Let X_t be a stationary diffusion process with state space $\mathbb{X}$, generator $\mathcal{L}$, invariant measure $\mu(dx)$ and let $V^f(x)$, $D^{f,g}(x)$ given by* (2.33) *and* (2.34)*, respectively. Then*

$$\frac{1}{2}\int D^{f,f}\mu(dx) = \int_0^\infty \mathbb{E}\Big(V^f(X_t)V^f(X_0)\Big)\,dt. \tag{2.35}$$

Proof. We will use the notation $(\cdot,\cdot)_\mu$ for the inner product in $L^2(\mathbb{X},\mu)$. First we note that

$$\frac{1}{2}\int D^{f,f}\mu(dx) = (-\mathcal{L}f, f)_\mu := D_{\mathcal{L}}(f), \tag{2.36}$$

where $D_{\mathcal{L}}(f)$ is the *Dirichlet form* associated with the generator $\mathcal{L}$. In view of (2.36), formula (2.35) becomes

$$D_{\mathcal{L}}(f) = \int_0^\infty \mathbb{E}\Big(V^f(X_t)V^f(X_0)\Big)\,dt. \tag{2.37}$$

Now we use (2.25), together with the fact that

$$\int_0^\infty e^{\mathcal{L}t}\cdot\,dt = (-\mathcal{L})^{-1}$$

to obtain

$$\int_0^\infty \kappa_{A,B}(t)\,dt = ((-\mathcal{L})^{-1}A, B)_\mu.$$

We set now $A = B = V^f = \mathcal{L}f$ in the above formula to obtain (2.37) from which (2.35) follows. □

Remark 2.10. *In the reversible case we can show that*

$$\frac{1}{2}\int D^{f,g}\mu(dx) = \int_0^\infty \mathbb{E}\Big(V^f(X_t)V^g(X_0)\Big)\,dt. \tag{2.38}$$

In the reversible case (i.e. $\mathcal{L}$ being a selfadjoint operator in $\mathcal{H} := L^2(\mathbb{X},\mu)$) the formal calculations presented in the above proof can be justified rigorously using functional calculus and spectral theory. See Exercise 7

Example 2.11. *Consider the diffusion process* (2.39) *from Section* **??***:*

$$dX_t = b(X_t)\,dt + \sigma(X_t)\circ dW_t, \tag{2.39}$$

where the noise is interpreted in the Stratonovich sense. The generator is

$$\mathcal{L}\cdot = b(x)\cdot\nabla + \frac{1}{2}\nabla\cdot\left(A(x)\nabla\cdot\right),$$

where $A(x) = (\sigma\sigma^T)(x)$. We assume that the diffusion process has a unique invariant distribution which is the solution of the stationary Fokker-Planck equation

$$\mathcal{L}^*\rho = 0. \tag{2.40}$$

The stationary process X_t (i.e. $X_0 \sim \rho(x)dx$) is reversible provided that condition (**??**) *holds:*

$$b(x) = \frac{1}{2}A(x)\nabla \log \rho(x). \tag{2.41}$$

Let $f = x_i$, $g = x_j$. We calculate

$$V^{x_i}(x) = \mathcal{L}x_i = b_i + \frac{1}{2}\partial_k A_{ik},\ i = 1, \dots d. \tag{2.42}$$

We use the detailed balance condition (2.41) *and* (2.36) *to calculate*

$$\begin{aligned}
\frac{1}{2}\int D^{x_i,x_j}\mu(dx) &= (-\mathcal{L}x_i, x_j)_\mu \\
&= -\int \left(b_i(x) + \frac{1}{2}\partial_k A_{ik}(x)\right) x_j \rho(x)\, dx \\
&= -\frac{1}{2}\int \left(A_{ik}\partial_k\rho(x) + \partial_k A_{ik}(x)\rho(x)\right) x_j\, dx \\
&= \frac{1}{2}\int A_{ij}(x)\rho(x)\, dx.
\end{aligned}$$

The Green-Kubo formula (2.35) *gives:*

$$\frac{1}{2}\int A_{ij}(x)\rho(x)\, dx = \int_0^{+\infty} \mathbb{E}\Big(V^{x_i}(X_t)V^{x_j}(X_0)\Big)\, dt, \tag{2.43}$$

where the drift $V^{x_i}(x)$ is given by (**??**).

2.4 Discussion and Bibliography

.

Linear response theory and the fluctuation-dissipation theorem form the cornerstones of non-equilibrium statistical mechanics. These topics can be found in any book on non-equilibrium statistical mechanics such as [28, 41, 3, 50, 34]. An earlier reference is [6]. An early review article is [27].

In Section 2.1 we considered stationary processes whose invariant density has a smooth density with respect to Lebesgue measure. This excludes several interesting problems such as chaotic dynamical systems or stochastic PDEs. Linear response theory for deterministic dynamical systems is reviewed in [45] and for stochastic PDEs in [15]. Rigorous results on linear response theory and the fluctuation-dissipation theorem for Markov processes are presented in [7]. There is a very large literature on the mathematical justification of linear response theory, the fluctuations dissipation theory and the Green-Kubo formula. Our approach on the Green-Kubo formula in Section 2.3 and, in particular, Theorem 2.9 is based on [23, 48]. See also [22].

Formulas of the form (2.31) for the diffusion coefficient can be justified rigorously using tools either from stochastic analysis (the martingale central limit theorem) or the theory of partial differential equations (homogenization theory). The diffusion coefficient for reversible diffusions (together with the functional central limit theorem) is proved in [24]. Einstein's formula for the diffusion coefficient of a Brownian particle in a periodic potential is justified rigorously in [44].

Linear response theory and the fluctuation-dissipation theorem have a found a wide range of applications. Examples include climate modeling [31] and galactic dynamics [4, Ch. 5].

Linear response theory, the fluctuation–dissipation theorem and Green–Kubo formulas are important topics in quantum non-equilibrium statistical mechanics. See, for example [17, 18] and the references therein. See also [34].

2.5 Exercises

1. Let X_t be the solution of (2.8) and assume that we add a weak external forcing to both the drift and the noise. Write down the equation for the perturbed dynamics and the formulas for $\mathcal{L}^1$ and D.

2. Calculate higher order terms in the expansion (2.14). Use this in order to calculate higher order terms in the calculation of expectation values of observables.

3. Let X_t be a stationary Markov process with state space $\mathbb{X}$, generator $\mathcal{L}$ and invariant measure μ and let $f, g \in D(\mathcal{L})$ and $fg \in D(\mathcal{L})$. Show that

$$\lim_{h\to 0} \frac{1}{h}\mathbb{E}\Big((f(X_t)-f(X_0)(g(X_t)-g(X_0)\Big|X_0 = x\Big) = \mathcal{L}_0(fg)(x)-(g\mathcal{L}f)(x)-(f\mathcal{L}g)(x) \tag{2.44}$$

in $L^1(\mathbb{X}, \mu)$.

4. Let $X_t \in R^d$ be a dynamical system at equilibrium at $t = -\infty$, which is perturbed away from equilibrium by a weak external force $F(t)$. Let $A(x)$ be a scalar phase space function and consider the linear response relation

$$\Delta A(t) = \int_R \gamma(s) F(t-s)\, ds, \tag{2.45}$$

where $\Delta A(t) = \langle A(X_t)\rangle - \langle A(X_t)\rangle_{eq}$. The *causality principle* implies that

$$\gamma(t) = 0, \quad \text{for } t < 0. \tag{2.46}$$

Assume that $\gamma(t) \in L^1(\mathbb{R})$.

(a) Show that the linear response relation (2.45) can be written in the form

$$\widehat{\Delta A}(\omega) = \widehat{\gamma}(\omega)\widehat{F}(\omega), \tag{2.47}$$

where $\widehat{f}(\omega)$ denotes the Fourier transform of a function $f(t)$ (we assume that all Fourier transforms in (2.47) exist). The Fourier transform of the response function $\widehat{\gamma}(\omega)$ is called the *susceptibility*.

(b) Show that the causality principle (2.46) implies that $\widehat{\gamma}(\omega),\ \omega \in \mathbb{C}$ is an analytic function in the upper half of the complex half plane.

(c) Assume furthermore that $\lim_{|\omega|\to+\infty} \frac{1}{|\omega|}\gamma(\omega) = 0$. Apply Cauchy's integral theorem to the function

$$f(\omega) = \frac{\widehat{\gamma}(\omega)}{\omega - \zeta},$$

where $\zeta \in \mathbb{R}$ and use the residue theorem to prove the *Kramers-Kronig relations*

$$\gamma_R(\zeta) = \frac{1}{\pi}\mathcal{P}\int_{\mathbb{R}} \frac{\gamma_I(\omega)}{\omega - \zeta}\, d\omega, \tag{2.48a}$$

$$\gamma_I(\zeta) = -\frac{1}{\pi}\mathcal{P}\int_{\mathbb{R}} \frac{\gamma_R(\omega)}{\omega - \zeta}\, d\omega, \tag{2.48b}$$

where $\widehat{\gamma}(\omega) = \gamma_R(\omega) + i\gamma_I(\omega)$ and $\mathcal{P}$ denotes the Cauchy principal value. (Hint:integrate the function $f(\omega)$ along $\mathbb{R}$ and a semicircle in the upper half plane, avoiding the point $\zeta \in \mathbb{R}$ with a small semicircle of radius r in the upper half plane).

(d) Use the fact that $\gamma(t)$ is a real valued function to obtain the alternative formulas

$$\gamma_R(\zeta) = \frac{2}{\pi}\mathcal{P}\int_0^\infty \frac{\omega\gamma_I(\omega)}{\omega^2-\zeta^2}\,d\omega, \tag{2.49a}$$

$$\gamma_I(\zeta) = -\frac{1}{\pi}\mathcal{P}\int_{\mathbb{R}} \frac{\zeta\gamma_R(\omega)}{\omega^2-\zeta^2}\,d\omega. \tag{2.49b}$$

More information about the Kramers-Kronig relations can be found in [6, Sec. VIII.3], [41, Sec. XI.1.2].

5. Let A and Σ strictly positive and positive, respectively $d\times d$ matrices and consider the linear SDE

$$dX_t = -AX_t\,dt + \sqrt{2\Sigma}\,dW_t \tag{2.50}$$

(a) Consider a weak external forcing. Calculate the response function. Use this to calculate the equilibrium autocorrelation matrix

$$\langle x(t)\otimes x(0)\rangle_{eq}.$$

(b) Calculate the susceptibilities corresponding to the response functions $R_{\mathcal{L}_0,x_i}(t)$ (see Exercise 4).

(c) Consider weak fluctuations in the diffusion matrix Σ. Calculate the response function and the equilibrium autocorrelation function of the (appropriately defined) energy.

6. Use (2.25) to prove (2.27).

7. Let $\mathcal{L}$ be the generator of a reversible diffusion process. Use the spectral theorem for self-adjoint operators to provide a rigorous proof of (2.38).

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