CRITICAL DYNAMICS
A field theory approach to equilibrium and non-equilibrium scaling behavior

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To Karin, with love.

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Stochastic dynamics

In this chapter, we develop the basic tools for our study of dynamic critical phenomena. We introduce dynamic correlation, response, and relaxation functions, and explore their general features. In the linear response regime, these quantities can be expressed in terms of equilibrium properties. A fluctuation-dissipation theorem then relates dynamic response and correlation functions. Under more general non-equilibrium conditions, we must resort to the theory of stochastic processes. The probability $P_1(x,t)$ of finding a certain physical configuration x at time t is governed by a master equation. On the level of such a 'microscopic' description, we discuss the detailed-balance conditions which guarantee that $P_1(x,t)$ approaches the probability distribution of an equilibrium statistical ensemble as $t \to \infty$. Taking the continuum limit for the variable(s) x, we are led to the Kramers–Moyal expansion, which often reduces to a Fokker–Planck equation. Three important examples elucidate these concepts further, and also serve to introduce some calculational methods; these are biased one-dimensional random walks, a simple population dynamics model, and kinetic Ising systems. We then venture towards a more 'mesoscopic' viewpoint which focuses on the long-time dynamics of certain characteristic, 'relevant' quantities. Assuming an appropriate separation of time scales, the remaining 'fast' degrees of freedom are treated as stochastic noise. As an introduction to these concepts, the Langevin–Einstein theory of free Brownian motion is reviewed, and the associated Fokker–Planck equation is solved explicitly. Our considerations are then generalized to Brownian particles in an external potential, leading to the Smoluchowski equation for the probability distribution. At last, some general properties of Langevin–type stochastic differential equations are listed. Specifically, we note the sufficient conditions for the system to asymptotically approach thermal equilibrium, among them Einstein's relation for the relaxation constant and the strength of the thermal noise.

2.1 Dynamic response and correlation functions

As yet, there exists no unifying description of systems far from thermal equilibrium in terms of macroscopic thermodynamic variables akin to the spectacularly successful statistical ensemble approach in the equilibrium theory. For such inherently dynamical situations, we generally either need to solve the complete set of microscopic equations of motion, which is rarely feasible, or try and obtain an at least mesoscopic description through appropriate coarse-graining. However, the situation much improves in the *linear response* regime, where an equilibrium system is only slightly perturbed by a weak time-dependent potential. Macroscopic averages in the system then deviate from their stationary values only linearly in the external field, and the corresponding dynamic response functions are fully characterized by its *equilibrium* properties. Moreover, the dynamic correlation functions and susceptibilities are related through a *fluctuation-dissipation theorem*. Linear response theory thus sets the equilibrium baseline for the discussion of dynamic correlations under more general non-equilibrium conditions. Since our aim is to cover quantum critical phenomena as well, we employ the language and formalism of quantum statistical mechanics in this section. In fact, some derivations are actually facilitated in the quantum formalism.[1]

2.1.1 Dynamic correlation functions

In *quantum statistical mechanics*, $\langle A\rangle = \mathrm{Tr}(\rho A)$ denotes the ensemble average of an observable A with respect to a normalized density matrix (statistical operator) $\rho = \sum_j p_j |\psi_j\rangle\langle\psi_j|$, $\mathrm{Tr}\,\rho = \sum_j p_j = 1$. The orthonormal quantum states $|\psi_j\rangle$, $\langle\psi_i|\psi_j\rangle = \delta_{ij}$, are subject to *Schrödinger's equation* with the system's Hamiltonian H,

$$i\hbar \frac{\partial|\psi_j(t)\rangle}{\partial t} = H(t)\,|\psi_j(t)\rangle \ . \tag{2.1}$$

We write its formal solution as $|\psi_j(t)\rangle = U(t,t_0)|\psi_j(t_0)\rangle$, introducing the unitary time evolution operator $U(t,t_0)$, $U(t,t_0)^\dagger = U(t,t_0)^{-1}$. It obviously satisfies the Schrödinger equation as well,

$$i\hbar \frac{\partial U(t,t_0)}{\partial t} = H(t)\,U(t,t_0) \ , \tag{2.2}$$

with the initial condition $U(t_0,t_0) = 1$. Thus, both the density matrix $\rho(t)$ and the average $\langle A(t)\rangle = \mathrm{Tr}[\rho(t)A]$ are in general time-dependent quantities. Alternatively, one may employ the *Heisenberg picture* with time-dependent

[1] This section builds on the expositions in Chaikin and Lubensky (1995), Cowan (2005), Schwabl (2008), and Van Vliet (2010).

operators $A(t) = U(t,t_0)^\dagger A(t_0) U(t,t_0)$. Using the cyclic invariance of the trace, we then obtain $\langle A(t)\rangle = \mathrm{Tr}[\rho(t_0)A(t)]$. For conservative systems with a stationary Hamiltonian H, Eq. (2.2) is solved by $U(t,t_0) = e^{-iH(t-t_0)/\hbar}$, and $A(t)$ obeys *Heisenberg's equation of motion*

$$\frac{dA(t)}{dt} = \frac{i}{\hbar}\Big[H, A(t)\Big] + \frac{\partial A(t)}{\partial t} \ , \tag{2.3}$$

where the last term stems from any explicit time dependence of the operator A in the Schrödinger representation, transformed into the Heisenberg picture. We can now readily proceed to define a *correlation function* of two observables A and B at different times t and t':

$$C_{AB}(t,t') = \langle A(t)B(t')\rangle = \mathrm{Tr}\Big[\rho(t_0)A(t)B(t')\Big] \ . \tag{2.4}$$

In *classical* statistical mechanics, ρ is to be interpreted as a phase space trajectory density, and the trace becomes an integral over all generalized coordinates and conjugate momenta. The commutator in Eq. (2.3) is to be replaced with the Poisson bracket, $\frac{i}{\hbar}[H,A] \to \{H,A\}$. In any case, in *thermal equilibrium* $\rho(H)$ becomes a function of the Hamiltonian only (and perhaps additional conserved quantities), and therefore commutes with $U(t,0) = e^{-iHt/\hbar}$. Upon invoking the cyclic invariance of the trace once again, we find (setting $t_0 = 0$)

$$\begin{aligned} C_{AB}(t,t') &= \mathrm{Tr}\left(\rho(H)\, e^{iHt/\hbar} A\, e^{-iH(t-t')/\hbar} B\, e^{-iHt'/\hbar}\right) \\ &= \mathrm{Tr}\left(\rho(H)\, e^{iH(t-t')/\hbar} A\, e^{-iH(t-t')/\hbar} B\right) = C_{AB}(t-t',0) \\ &= \mathrm{Tr}\left(\rho(H)\, A\, e^{-iH(t-t')/\hbar} B\, e^{iH(t-t')/\hbar}\right) = C_{AB}(0,t'-t) \ . \end{aligned} \tag{2.5}$$

Consequently, upon defining the temporal Fourier transform via

$$A(t) = \frac{1}{2\pi}\int A(\omega)\, e^{-i\omega t}\, d\omega \ , \quad A(\omega) = \int A(t)\, e^{i\omega t}\, dt \ , \tag{2.6}$$

we obtain

$$\big\langle A(\omega)B(\omega')\big\rangle = C_{AB}(\omega)\, 2\pi\delta(\omega+\omega') \ , \tag{2.7}$$

where $C_{AB}(\omega)$ is the Fourier transform of $C_{AB}(t) = C_{AB}(t,0)$. The relation (2.7) is valid whenever *time translation invariance* holds. In this case, obviously $\langle A(t)\rangle = \langle A\rangle$ is independent of t, and $\langle A(\omega)\rangle = \langle A\rangle\, 2\pi\delta(\omega)$.

In the equilibrium canonical ensemble,

$$\rho(H) = \frac{1}{Z(T)}\, e^{-H/k_{\mathrm{B}}T} \ , \quad Z(T) = \mathrm{Tr}\, e^{-H/k_{\mathrm{B}}T} \ , \tag{2.8}$$

we may write

$$C_{AB}(t) = \frac{1}{Z(T)}\ \mathrm{Tr}\left(e^{-H/k_\mathrm{B}T}\, e^{iHt/\hbar} A\, e^{-iHt/\hbar} B\right) \tag{2.9}$$
$$= \frac{1}{Z(T)} \sum_{n,m} e^{-E_n/k_\mathrm{B}T}\, e^{i(E_n-E_m)t/\hbar}\, \langle n|A|m\rangle\langle m|B|n\rangle\ ,$$

where we have inserted a complete set of energy eigenstates $|n\rangle$ with eigenvalues E_n: $H|n\rangle = E_n|n\rangle$, $\sum_n |n\rangle\langle n| = 1$, and used the same basis for performing the trace, $\mathrm{Tr}\, A = \sum_n \langle n|A|n\rangle$. A Fourier transform then yields the *spectral representation*

$$C_{AB}(\omega) = \frac{2\pi\hbar}{Z(T)} \sum_{n,m} e^{-E_n/k_\mathrm{B}T} \langle n|A|m\rangle\langle m|B|n\rangle\, \delta(E_n - E_m + \hbar\omega)\ . \tag{2.10}$$

Upon exchanging the summation indices $m \leftrightarrow n$ and exploiting the delta function, we see that

$$C_{BA}(-\omega) = C_{AB}(\omega)\, e^{-\hbar\omega/k_\mathrm{B}T}\ . \tag{2.11}$$

Scattering experiments directly probe dynamic correlation functions. For example, in inelastic light scattering, the coherent scattering cross section is proportional to $S_c(q,\omega)$, the Fourier transform of the normalized *density-density correlation function*

$$S_c(q,t) = \frac{1}{N}\langle n(q,t) n(-q,0)\rangle\ . \tag{2.12}$$

Here, $n(x,t) = \sum_{i=1}^N \delta\Big(x - x_i(t)\Big)$ denotes the density operator for an N-particle system, and $n(q,t) = \int n(x,t)\, e^{-iqx} d^d x = \sum_{i=1}^N e^{-iqx_i(t)}$ its spatial Fourier transform. Eq. (2.11) now reads $S_c(-q,-\omega) = S_c(q,\omega)\, e^{-\hbar\omega/k_\mathrm{B}T}$ and has an immediate physical implication: The intensity of the 'anti-Stokes' emission lines ($\omega < 0$) is suppressed by a temperature-dependent detailed-balance factor as compared with the 'Stokes' absorption lines ($\omega > 0$). Indeed, as $T \to 0$, the system is in the ground state, and no emission is possible at all. In the classical limit $k_\mathrm{B}T \gg \hbar\omega$, the absorption and emission line strengths become equal. The equal-time correlation

$$S_c(q) = S_c(q, t=0) = \frac{1}{N}\left\langle |n(q,0)|^2 \right\rangle \tag{2.13}$$

is called the static *structure factor*. Notice that $S_c(q=0,\omega) = N\, 2\pi\delta(\omega)$.

2.1.2 Dynamic susceptibilities and relaxation functions

Another means to investigate dynamic properties of a physical system is a *relaxation* experiment. Such a situation may be described theoretically by adding to the stationary Hamiltonian H_0 a time-dependent term of the form $H'(t) = -F(t)B$, where the function $F(t)$ denotes an external 'force' that couples to the system via the Hermitean operator $B = B^\dagger$. This interaction induces a deviation $\delta A(t) = \langle A(t)\rangle - \langle A\rangle_0$ of the ensemble average for the observable A from its time-independent unperturbed value $\langle A\rangle_0$, which is determined by the equilibrium density matrix $\rho(H_0)$. This change can be formally expanded in terms of powers of $F(t)$,

$$\delta A(t) = \int \chi_{AB}(t-t')F(t')dt' + \frac{1}{2}\int \chi^{(2)}_{ABB}(t-t',t-t'')F(t')F(t'')dt'dt'' + \ldots , \tag{2.14}$$

which defines the (linear) *dynamic susceptibility (response function)*

$$\chi_{AB}(t-t') = \left.\frac{\delta\langle A(t)\rangle}{\delta F(t')}\right|_{F=0} , \tag{2.15}$$

and the (second-order) *non-linear response function*

$$\chi^{(2)}_{ABB}(t-t',t-t'') = \left.\frac{\delta^2\langle A(t)\rangle}{\delta F(t')\,\delta F(t'')}\right|_{F=0} , \tag{2.16}$$

respectively. Higher-order non-linear response functions, perhaps involving couplings to additional operators, follow by means of straightforward generalization. The stationarity of H_0 implies that the susceptibilities must be functions of the time differences $t-t'$, $t-t''$, etc. only.

It is important to realize that the dynamic response functions are fully determined by the *equilibrium* properties of the system. For a weak field $F(t)$, we expect $|\delta A(t)/\langle A\rangle_0| \ll 1$, and taking into account only the linear response should provide an adequate description. If the external perturbation is *instantaneous*, i.e., represented by a delta peak at time $t = 0$: $F(t) = F\delta(t)$, the linear response simply becomes $\delta A(t) = 0$ for $t < 0$, and $\delta A(t) = F\chi_{AB}(t)$ for $t \geq 0$, see Fig. 2.1(a). Generally, as a consequence of *causality* (effects cannot precede their causes), the susceptibilities should be proportional to the product of Heaviside step functions of their arguments, $\chi_{AB}(t-t') \propto \Theta(t-t')$, $\chi^{(2)}_{ABB}(t-t',t-t'') \propto \Theta(t-t')\Theta(t-t'')$, and so forth. Thus, we may write for the linear response

$$\delta A(t) = \int_{-\infty}^{t} \chi_{AB}(t-t')F(t')\,dt' = \int_0^\infty \chi_{AB}(s)F(t-s)\,ds , \tag{2.17}$$

where $s = t-t'$. The convolution theorem yields for the Fourier transform

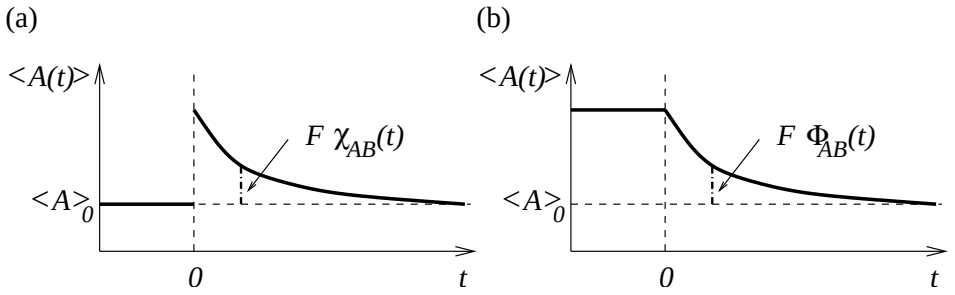

Fig. 2.1. Relaxation of the average $\langle A(t)\rangle$ towards its equilibrium value $\langle A\rangle_0$: (a) following an instantaneous perturbation F at $t = 0$, and (b) after switching off the external field F at $t = 0$; the deviation from $\langle A\rangle_0$ in these situations is given by the dynamic response and Kubo relaxation functions, respectively.

of Eq. (2.14): $\langle A(\omega)\rangle = \langle A\rangle_0\, 2\pi\delta(\omega) + \chi_{AB}(\omega)F(\omega) + O(F^2)$, or

$$\chi_{AB}(\omega) = \int_0^\infty \chi_{AB}(t)\, e^{i\omega t}\, dt = \left.\frac{\partial\langle A(\omega)\rangle}{\partial F(\omega)}\right|_{F=0} . \tag{2.18}$$

Hence, the Laplace transform of the dynamic susceptibility $\chi_{AB}(\omega)$ directly provides the response of the Fourier component $\langle A(\omega)\rangle$ to the external perturbation at the same frequency.

Another typical situation is that a perturbation existing for all previous times is switched off at $t = 0$, $F(t) = F\,\Theta(-t)$. The system's linear response may then be written as $\delta A(t) = F\,\Phi_{AB}(t)$, see Fig. 2.1(b), which defines *Kubo's relaxation function* $\Phi_{AB}(t)$. Comparison with Eq. (2.17) immediately gives the relation

$$\Phi_{AB}(t) = \begin{cases} \int_0^\infty \chi_{AB}(s)\, ds = \chi_{AB}(\omega = 0) & t \le 0 \\ \int_t^\infty \chi_{AB}(s)\, ds & t > 0 \end{cases} . \tag{2.19}$$

Thus, the Kubo relaxation function and linear dynamic susceptibility are by no means independent quantities, but $\chi_{AB}(t) = -d\Phi_{AB}/dt$ for $t > 0$, with the boundary conditions $\Phi_{AB}(t = 0) = \chi_{AB}(\omega = 0)$ and $\Phi_{AB}(t \to \infty) = 0$. Integration by parts then yields for the Laplace transform

$$\Phi_{AB}(\omega) = \int_0^\infty \Phi_{AB}(t)\, e^{i\omega t}\, dt = \frac{1}{i\omega}\Big[\chi_{AB}(\omega) - \chi_{AB}(\omega = 0)\Big] . \tag{2.20}$$

It therefore suffices to discuss the properties of either the linear response function $\chi_{AB}(\omega)$ or the relaxation function $\Phi_{AB}(\omega)$ (see Probs. 2.1 and 2.2).

Let us now consider the analytic continuation of $\chi_{AB}(\omega)$ to complex frequencies z,

$$\chi_{AB}(z) = \int \chi_{AB}(t)\, e^{izt}\, dt . \tag{2.21}$$

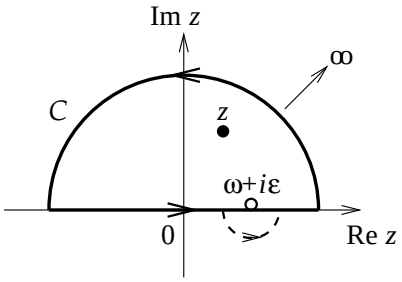

Fig. 2.2. Integration contour $\mathcal{C}$ in the complex frequency plane for the derivation of the Kramers–Kronig relations for the dynamic susceptibility $\chi_{AB}(z)$. The dashed semicircle represents the required contour deformation as the frequency $z = \omega + i\varepsilon$ approaches the real axis ($\varepsilon \downarrow 0$).

Causality demands $\chi_{AB}(t)$ to vanish for $t < 0$. Therefore, $\chi_{AB}(z)$ has to be analytic in the upper complex half-plane ($\mathrm{Im}\, z > 0$). For any integration contour $\mathcal{C}$ in the analytic region, Cauchy's integral theorem states that

$$\chi_{AB}(z) = \frac{1}{2\pi i} \int_{\mathcal{C}} \frac{\chi_{AB}(z')}{z' - z}\, dz' \ . \tag{2.22}$$

We choose the integration contour as depicted in Fig. 2.2, and assume that $\chi_{AB}(z)$ decays sufficiently fast as $|z| \gg 1$ for the line integral along the semicircle in the upper half-plane to vanish when its radius is pushed to infinity. Eq. (2.22) then reduces to an integral over the entire real axis,

$$\chi_{AB}(z) = \frac{1}{2\pi i} \int \frac{\chi_{AB}(\omega')}{\omega' - z}\, d\omega' \ . \tag{2.23}$$

Upon approaching real frequencies $z = \omega + i\varepsilon$, $\varepsilon \downarrow 0$, we need to deform the integration contour as indicated by the dashed path in Fig. 2.2. The integral now becomes a sum of the Cauchy principal value and the contour integral of the dashed infinitesimal semicircle, which contributes precisely one half of the residue of the pole at $\omega' = \omega$:

$$\lim_{\varepsilon \downarrow 0} \chi_{AB}(\omega + i\varepsilon) = \frac{1}{2\pi i}\, \mathcal{P} \int \frac{\chi_{AB}(\omega')}{\omega' - \omega}\, d\omega' + \frac{1}{2}\, \chi_{AB}(\omega) \ ,$$

or

$$\chi_{AB}(\omega) = \frac{1}{i\pi}\, \mathcal{P} \int \frac{\chi_{AB}(\omega')}{\omega' - \omega}\, d\omega' \ . \tag{2.24}$$

The preceding limiting procedure is encoded in the formal identity

$$\lim_{\varepsilon \downarrow 0} \frac{1}{x \mp i\varepsilon} = \mathcal{P}\, \frac{1}{x} \pm i\pi\, \delta(x) \ . \tag{2.25}$$

Setting $x = \omega' - \omega$, and inserting (2.25) into (2.23) directly results in

Eq. (2.24). Separating into real and imaginary parts, we arrive at the *Kramers–Kronig relations*

$$\mathrm{Re}\,\chi_{AB}(\omega) = \frac{1}{\pi}\,\mathcal{P}\!\int \frac{\mathrm{Im}\,\chi_{AB}(\omega')}{\omega'-\omega}\,d\omega'\ , \tag{2.26}$$

$$\mathrm{Im}\,\chi_{AB}(\omega) = -\frac{1}{\pi}\,\mathcal{P}\!\int \frac{\mathrm{Re}\,\chi_{AB}(\omega')}{\omega'-\omega}\,d\omega'\ . \tag{2.27}$$

As a consequence of causality, the real and imaginary parts of the dynamic susceptibility $\chi_{AB}(\omega)$ are intimately connected, and either can be computed if the other happens to be known at all (real) frequencies.

2.1.3 Linear response and fluctuation-dissipation theorem

We now proceed to express the linear susceptibility in terms of a dynamic correlation function. Within the framework of *linear* response, we merely need to apply first-order time-dependent perturbation theory. The total Hamiltonian is $H(t) = H_0 + H'(t) = H_0 - F(t)B$, where we assume that $F(t) = 0$ for $t \le t_0$. As we presume to know the solution with the unperturbed stationary Hamiltonian H_0, it is beneficial to transform to the *interaction representation* via $U(t,t_0) = e^{-iH_0(t-t_0)/\hbar}\,U'(t,t_0)$. By means of Eq. (2.2), we see that $U'(t,t_0)$ obeys the equation of motion

$$\begin{aligned} i\hbar\,\frac{\partial U'(t,t_0)}{\partial t} &= e^{iH_0(t-t_0)/\hbar}\left[i\hbar\,\frac{\partial U(t,t_0)}{\partial t} - H_0\,U(t,t_0)\right] \\ &= e^{iH_0(t-t_0)/\hbar}\,H'(t)\,e^{-iH_0(t-t_0)/\hbar}\,U'(t,t_0) = H'_I(t)\,U'(t,t_0)\ , \end{aligned} \tag{2.28}$$

where $H'_I(t)$ denotes the perturbing Hamiltonian in the interaction representation. The equivalent integral equation

$$U'(t,t_0) = 1 + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\ H'_I(t')\,U'(t',t_0) \tag{2.29}$$

is readily solved iteratively,

$$U'(t,t_0) = 1 + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\,H'_I(t') + \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\,H'_I(t')\,H_I(t'')\ldots\ . \tag{2.30}$$

This expression may be nicely rewritten by means of a time-ordered product. However, we just require the first-order contribution, which we insert into

$$\begin{aligned} \langle A(t)\rangle &= \mathrm{Tr}\,[\rho_0(t_0)\,A(t)] = \mathrm{Tr}\left[\rho_0(t_0)\,U(t,t_0)^\dagger A(t_0)\,U(t,t_0)\right] \\ &= \mathrm{Tr}\left[\rho_0(t_0)\,e^{iH_0(t-t_0)/\hbar}\,A(t_0)\,e^{-iH_0(t-t_0)/\hbar}\right] \\ &\quad + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\,\mathrm{Tr}\left(\rho_0(t_0)\left[e^{iH_0(t-t_0)/\hbar}\,A(t_0)\,e^{-iH_0(t-t_0)/\hbar}\,,\,H'_I(t')\right]\right). \end{aligned}$$

The first term represents the unperturbed average $\langle A\rangle_0$. For the second term we recall Eq. (2.28), whereupon we arrive at

$$\delta A(t) = \frac{i}{\hbar}\int_{t_0}^{t} dt' \,\Big\langle \Big[e^{iH_0(t-t_0)/\hbar}\, A(t_0)\, e^{-iH_0(t-t_0)/\hbar}\,, \\ e^{iH_0(t'-t_0)/\hbar}\, B(t_0)\, e^{-iH_0(t'-t_0)/\hbar}\Big]\Big\rangle_0 F(t') \;. \tag{2.31}$$

To this order, the commutator is just $[A(t), B(t')]$. Taking the limit $t_0 \to -\infty$, we at last find upon comparison with the definition in Eq. (2.14) that the linear susceptibility is given by a retarded commutator,

$$\chi_{AB}(t-t') = \frac{i}{\hbar}\Big\langle [A(t), B(t')]\Big\rangle_0 \Theta(t-t') \;, \tag{2.32}$$

where the ensemble average is taken with respect to the *equilibrium* Hamiltonian H_0 (we shall henceforth drop the index '0').

This fundamental result contains the antisymmetric combination

$$\chi''_{AB}(t) = \frac{1}{2\hbar}\Big\langle [A(t), B(0)]\Big\rangle = \frac{1}{2\hbar}\Big[C_{AB}(t) - C_{BA}(-t)\Big] = -\chi''_{BA}(-t) \;, \tag{2.33}$$

whence $\chi''_{AB}(\omega) = -\chi''_{BA}(-\omega)$. The relation (2.11) now yields the important quantum-mechanical *fluctuation-dissipation theorem* (FDT)

$$\chi''_{AB}(\omega) = \frac{1}{2\hbar}\Big(1 - e^{-\hbar\omega/k_{\rm B}T}\Big)\, C_{AB}(\omega) \;. \tag{2.34}$$

In the *classical limit* $\hbar\omega/k_{\rm B}T \ll 1$, we may expand the exponential to obtain

$$\chi''_{AB}(\omega) = \frac{\omega}{2k_{\rm B}T}\; C_{AB}(\omega) \;, \tag{2.35}$$

$$\chi_{AB}(t) = 2i\,\chi''_{AB}(t)\,\Theta(t) = -\,\frac{\Theta(t)}{k_{\rm B}T}\,\frac{dC_{AB}(t)}{dt} \;. \tag{2.36}$$

In order to compute its Fourier transform, we need the integral representation of the Heaviside step function,

$$\Theta(t) = \lim_{\varepsilon\downarrow 0}\int \frac{d\omega}{2\pi}\;\frac{i\,e^{-i\omega t}}{\omega + i\varepsilon} \;. \tag{2.37}$$

Indeed, for $t > 0$, convergence considerations enforce the closure of the integration path in the lower complex frequency half-plane, and the residue theorem yields $\Theta(t) = 1$, while for $t < 0$, the contour is to be closed in the upper half-plane where the integrand is analytic, and the integral vanishes. By means of the convolution theorem then

$$\chi_{AB}(\omega) = \lim_{\varepsilon\downarrow 0}\frac{1}{\pi}\int \frac{\chi''_{AB}(\omega')}{\omega' - \omega - i\varepsilon}\, d\omega' \;, \tag{2.38}$$

and upon inserting Eqs. (2.33) and (2.10), we arrive at the spectral representation for the dynamic response function,

$$\chi_{AB}(\omega) = \lim_{\varepsilon\downarrow 0} \frac{1}{Z(T)} \sum_{n,m} \langle n|A|m\rangle\langle m|B|n\rangle \, \frac{e^{-E_n/k_{\rm B}T} - e^{-E_m/k_{\rm B}T}}{E_m - E_n - \hbar(\omega + i\varepsilon)} \ . \quad (2.39)$$

In the classical limit, Eq. (2.38) reads

$$\chi_{AB}(\omega) = \lim_{\varepsilon\downarrow 0} \frac{1}{2\pi k_{\rm B}T} \int \frac{\omega' \, C_{AB}(\omega')}{\omega' - \omega - i\varepsilon} \, d\omega' \ , \quad (2.40)$$

and the *thermodynamic susceptibility* becomes

$$\chi_{AB} = \chi_{AB}(\omega = 0) = \frac{1}{k_{\rm B}T} \int \frac{d\omega}{2\pi} \, C_{AB}(\omega) = \frac{C_{AB}(t=0)}{k_{\rm B}T} = \frac{\langle AB\rangle}{k_{\rm B}T} \ . \quad (2.41)$$

Thus, we recover the classical *fluctuation-response theorem*, see Eq. (1.33). Applying the identity (2.25) to Eq. (2.38), we furthermore obtain

$$\chi_{AB}(\omega) = \chi'_{AB}(\omega) + i \, \chi''_{AB}(\omega) \ , \quad (2.42)$$

where

$$\chi'_{AB}(\omega) = \frac{1}{\pi} \, \mathcal{P} \int \frac{\chi''_{AB}(\omega')}{\omega' - \omega} \, d\omega' = \chi'_{BA}(-\omega) \ . \quad (2.43)$$

If $\chi''_{AB}(\omega)$ is real, this just represents the decomposition into real and imaginary parts and the Kramers–Kronig relation (2.26). This is certainly true in the case $B = A^\dagger$. Notice that $\chi'_{AA^\dagger}(\omega)$ and $\chi''_{AA^\dagger}(\omega)$ are symmetric and antisymmetric functions of ω, respectively. It is instructive to discuss the case of a periodic external perturbation with $F(t) = F\cos\omega t$. According to *Fermi's golden rule* of first-order time-dependent perturbation theory, the transition rate (as $t \to \infty$) from energy eigenstates $|n\rangle$ to $|m\rangle$ is

$$\Gamma_{n\to m}(\omega) = \frac{2\pi}{\hbar} \, F^2 \, |\langle m|A|n\rangle|^2 \left[\delta(E_m - E_n - \hbar\omega) + \delta(E_m - E_n + \hbar\omega)\right] . \quad (2.44)$$

For $\omega > 0$, the two terms here correspond to absorption and emission of an energy quantum $\hbar\omega$, respectively. In order to compute the total *dissipated power* at frequency ω, we have to multiply with the energy transfer $E_m - E_n$, and sum over all possible initial and final states, weighted with the canonical probability distribution for the initial states:

$$P(\omega) = \sum_{n,m} \frac{e^{-E_n/k_{\rm B}T}}{Z(T)} \, \Gamma_{n\to m}(\omega) \, (E_m - E_n) = 2\pi\omega F^2 \quad (2.45)$$

$$\times \sum_{n,m} \frac{e^{-E_n/k_{\rm B}T}}{Z(T)} \, |\langle m|A|n\rangle|^2 \Big[\delta(E_m - E_n - \hbar\omega) - \delta(E_m - E_n + \hbar\omega)\Big] .$$

Comparing with the spectral representation (2.10), we find

$$P(\omega) = \frac{\omega}{\hbar} F^2 \left[C_{AA^\dagger}(\omega) - C_{A^\dagger A}(-\omega) \right] = 2\omega F^2 \, \chi''_{AA^\dagger}(\omega) \; . \tag{2.46}$$

Therefore, $\chi''_{AA^\dagger}(\omega)$ describes the *dissipative* response to an external perturbation at frequency ω, which explains the term fluctuation-dissipation theorem for Eq. (2.34), while the real part of the dynamic susceptibility $\chi'_{AA^\dagger}(\omega)$ gives the *reactive* response. Inserting $F(t) = \frac{F}{2}(e^{i\omega t} + e^{-i\omega t})$ into Eq. (2.17), separating $\chi_{AA^\dagger}(\omega)$ into its real and imaginary parts, and exploiting their symmetries results in

$$\begin{aligned} \delta A(t) &= \frac{F}{2} \left[e^{-i\omega t} \chi_{AA^\dagger}(\omega) + e^{i\omega t} \chi_{AA^\dagger}(-\omega) \right] \\ &= F \left[\cos\omega t \, \chi'_{AA^\dagger}(\omega) + \sin\omega t \, \chi''_{AA^\dagger}(\omega) \right] \; . \end{aligned} \tag{2.47}$$

Both the reactive and dissipative response occur at the applied frequency, but the dissipative part acquires a phase shift of $\frac{\pi}{2}$.

Finally, we take n derivatives of Eq. (2.33) with respect to time:

$$\frac{d^n \chi''_{AB}(t)}{dt^n} = \int \frac{d\omega}{2\pi} \, \chi''_{AB}(\omega) \, (-i\omega)^n \, e^{-i\omega t} = \frac{1}{2\hbar} \left\langle \left[\frac{d^n A(t)}{dt^n}, B(0) \right] \right\rangle \; . \tag{2.48}$$

Via Heisenberg's equation of motion (2.3), the right-hand side can be recast in terms of n commutators with the Hamiltonian H. Setting $t = 0$ yields the *sum rules*

$$\begin{aligned} \int \frac{d\omega}{\pi} \, \omega^n \, \chi''_{AB}(\omega) &= \frac{i^n}{\hbar} \left\langle \left[\frac{d^n A(t)}{dt^n}, B(0) \right] \Big|_{t=0} \right\rangle \\ &= \frac{1}{\hbar^{n+1}} \left\langle \Big[\big[\ldots [A, H], \ldots, H \big], B \Big] \right\rangle \; , \end{aligned} \tag{2.49}$$

which provide *exact* relations for the frequency moments of the dissipative response (applications for the density response are treated in Prob. 2.3).

2.2 Stochastic processes

In situations far from thermal equilibrium, especially outside the linear response regime, the probability distribution for a physical system's accessible microstates will in general be a non-trivial function of time t. With prescribed time-independent boundary conditions, e.g., with a fixed particle or energy current running through the system, one expects it to reach a *non-equilibrium stationary state*, after a sufficiently long time has elapsed since its preparation. The identification and characterization of the ensuing

special stationary probability distributions and currents, as well as a quantitative description of the associated relaxation phenomena are among the central research goals of current non-equilibrium statistical mechanics.

To this end, we could in principle take recourse to a fully microscopic description, and solve the quantum-mechanical *von-Neumann equation*

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}\Big[H, \rho\Big] \ , \tag{2.50}$$

which follows immediately from the definition of the density matrix ρ and Schrödinger's equation (2.1), or its classical counterpart, namely *Liouville's equation* for the phase space density,

$$\frac{\partial \rho(t)}{\partial t} = -\Big\{H, \rho\Big\} \ , \tag{2.51}$$

where the Poisson bracket replaces the quantum-mechanical commutator. Notice that in both cases, the total time derivative (in the Heisenberg picture within the quantum framework) becomes $d\rho(t)/dt = 0$: Classically, this is just Liouville's theorem, and corresponds to overall probability conservation. However, such a microscopic approach is rarely feasible in practice. Instead, we may utilize our knowledge of the possible transitions between the microstates, and apply the mathematical theory of stochastic processes.[2] By means of coarse-graining, one might hope to subsequently arrive at equations for the time evolution of appropriate meso- or macroscopic variables.

2.2.1 Time-dependent probability distributions

Let us consider a random variable x, dependent on a real parameter t we call 'time'. We then refer to the ordered sequence $\{x(t_1), x(t_2), \ldots, x(t_n)\}$, with $t_1 \leq t_2 \leq \ldots \leq t_n$, as a *stochastic process* (Fig. 2.3). Next we introduce the n-point probability distribution P_n: The joint probability for the random variable x to assume a value in the interval $[x_1, x_1 + dx_1]$ at time t_1, a value in the interval $[x_2, x_2 + dx_2]$ at time t_2, etc., is given by $P_n(x_1, t_1; x_2, t_2; \ldots; x_n, t_n)\, dx_1 \ldots dx_n$. Its obvious properties are positivity: $P_n(x_1, t_1; x_2, t_2; \ldots; x_n, t_n) \geq 0$, and $P_n(\ldots x_i, t_i; \ldots; x_j, t_j; \ldots) = P_n(\ldots x_j, t_j; \ldots; x_i, t_i; \ldots)$, i.e., the ordering of the arguments is irrelevant. In addition, if we demand $\int dx_1 P_1(x_1, t_1) = 1$ and prescribe the *hierarchy rule*

$$\int dx_n\, P_n(x_1, t_1; \ldots; x_{n-1}, t_{n-1}; x_n, t_n) = P_{n-1}(x_1, t_1; \ldots; x_{n-1}, t_{n-1}) \ , \tag{2.52}$$

[2] Van Kampen (1981); see also Van Vliet (2010).

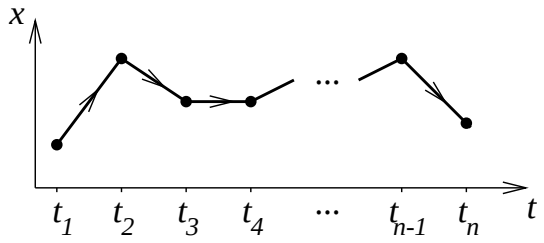

Fig. 2.3. A stochastic process as ordered time sequence of random variables $\{x(t_i)\}$.

we ensure proper normalization for all n-point probability distributions,

$$\int dx_1 \ldots \int dx_n \, P_n(x_1, t_1; \ldots; x_n, t_n) = 1 \ . \tag{2.53}$$

Time-dependent averages, moments, and correlations are defined via

$$\langle x(t_1) \ldots x(t_n) \rangle = \int dx_1 \ldots \int dx_n \, P_n(x_1, t_1; \ldots; x_n, t_n) \, x_1 \ldots x_n \ . \tag{2.54}$$

We call a stochastic process *stationary*, if time translation invariance holds, $P_n(x_1, t_1 + \tau; \ldots; x_n, t_n + \tau) = P_n(x_1, t_1; \ldots; x_n, t_n)$. Setting $\tau = -t_1$, we note $P_n(x_1, t_1; x_2, t_2; \ldots; x_n, t_n) = P_n(x_1, 0; x_2, t_2 - t_1; \ldots; x_n, t_n - t_1)$ in this case, whence $P_1(x)$ and $\langle x \rangle$ become time-independent, while for the n-point correlations $\langle x_1(t_1) \, x_2(t_2) \ldots x_n(t_n) \rangle = \langle x_1(0) \, x_2(t_2 - t_1) \ldots x_n(t_n - t_1) \rangle$.

Causal sequences can now be encoded through *conditional* probabilities. Let $P_{m|k}(x_{k+1}, t_{k+1}; \ldots; x_{k+m}, t_{k+m} | x_1, t_1; \ldots; x_k, t_k) \, dx_{k+1} \ldots dx_{k+m}$ indicate the probability of finding x in the intervals $[x_{k+1}, x_{k+1} + dx_{k+1}], \ldots, [x_{k+m}, x_{k+m} + dx_{k+m}]$ at the instances $t_{k+1}, \ldots, t_{k+m}$, respectively, *provided* it already appeared in $[x_1, x_1 + dx_1], \ldots, [x_k, x_k + dx_k]$ at $t_1, \ldots, t_k$. In terms of the n-point distributions, the conditional probabilities become

$$\begin{aligned} P_{m|k} \, (x_{k+1}, t_{k+1}; \ldots; x_{k+m}, t_{k+m} | x_1, t_1; \ldots; x_k, t_k) \\ = \frac{P_{k+m}(x_1, t_1; \ldots; x_{k+m}, t_{k+m})}{P_k(x_1, t_1; \ldots; x_k, t_k)} \ , \end{aligned} \tag{2.55}$$

and with Eq. (2.52) we obtain their normalization

$$\int dx_{k+1} \ldots dx_{k+m} \, P_{m|k} \, (x_{k+1}, t_{k+1}; \ldots; x_{k+m}, t_{k+m} | x_1, t_1; \ldots; x_k, t_k) = 1 \ . \tag{2.56}$$

If the first k outcomes $\{x_1(t_1), \ldots, x_k(t_k)\}$ do not influence the subsequent events $\{x_{k+1}(t_{k+1}), \ldots, x_{k+m}(t_{k+m})\}$, i.e.,

$$\begin{aligned} P_{m|k}(x_{k+1}, t_{k+1}; \ldots; x_{k+m}, t_{k+m} | x_1, t_1; \ldots; x_k, t_k) \\ = P_m(x_{k+1}, t_{k+1}; \ldots; x_{k+m}, t_{k+m}) \ , \end{aligned} \tag{2.57}$$

the event sequence $x_{k+1}, \ldots, x_{k+m}$ is said to be *statistically independent* of the preceding $x_1, \ldots, x_k$, and we infer

$$\begin{aligned} P_{k+m}(x_1, t_1; \ldots; x_{k+m}, t_{k+m}) \\ = P_k(x_1, t_1; \ldots; x_k, t_k)\, P_m(x_{k+1}, t_{k+1}; \ldots; x_{k+m}, t_{k+m}) \ . \end{aligned} \tag{2.58}$$

Thus, the random variables sets $\{x_1, \ldots, x_k\}$ and $\{x_{k+1}, \ldots, x_{k+m}\}$ are *not correlated*. For a *fully uncorrelated* stochastic process, with no memory at all to previous events, the n-point distribution factorizes completely, $P_n(x_1, t_1; \ldots; x_n, t_n) = \prod_{j=1}^{n} P_1(x_j, t_j)$.

Markov chains represent another special situation: Here, the value x_n of the random variable x at time t_n depends *only* on its values at the preceding instant t_{n-1}; i.e., there is short-term memory, but any recording of x wipes out the effects of the entire earlier history. Mathematically, the Markovian character means that

$$P_{1|n-1}(x_n, t_n | x_1, t_1; \ldots; x_{n-1}, t_{n-1}) = P_{1|1}(x_n, t_n | x_{n-1}, t_{n-1}) \ . \tag{2.59}$$

It is intuitively clear that a Markov process is fully determined by the initial configuration given by $P_1(x_1, t_1)$ and the sequence of intermediate *transition probabilities* $P_{1|1}(x_{j+1}, t_{j+1} | x_j, t_j)$. Indeed, using Eq. (2.55) and the Markovian property, one readily proves

$$\begin{aligned} P_n(x_1, t_1; \ldots; x_n, t_n) = P_{1|1}(x_n, t_n | x_{n-1}, t_{n-1}) \\ \times P_{1|1}(x_{n-1}, t_{n-1} | x_{n-2}, t_{n-2}) \ldots P_{1|1}(x_2, t_2 | x_1, t_1)\, P_1(x_1, t_1) \ . \end{aligned} \tag{2.60}$$

For example, for $t \le \bar{t} \le t'$ we can write

$$\begin{aligned} P_2(x, t; x', t') &= \int d\bar{x}\, P_3(x, t; \bar{x}, \bar{t}; x', t') \\ &= \int d\bar{x}\, P_{1|1}(x', t' | \bar{x}, \bar{t})\, P_{1|1}(\bar{x}, \bar{t} | x, t)\, P_1(x, t) \ ; \end{aligned}$$

dividing with $P_1(x, t)$ then yields the *Chapman–Kolmogorov equation*

$$P_{1|1}(x', t' | x, t) = \int d\bar{x}\, P_{1|1}(x', t' | \bar{x}, \bar{t})\, P_{1|1}(\bar{x}, \bar{t} | x, t) \ . \tag{2.61}$$

Its content is that the transition from x to x' can be split into intermediate steps $x \to \bar{x}$ and $\bar{x} \to x'$, and the second transition is independent of the origin of the first step. The associated probability is obtained by multiplying the separate transition probabilities, and integrating over all possible intermediate values $\bar{x}$.

A *Gaussian* stochastic process is fully characterized by the second moments, Eq. (2.54) for $n = 2$, because all higher correlations factorize, compare Eq. (1.104). One may then show that the factorization property of the

increments $\langle[x(t+\tau)-x(t)][x(t'+\tau)-x(t')]\rangle = \langle x(t+\tau)-x(t)\rangle\langle x(t'+\tau)-x(t')\rangle$ for $t \neq t'$ is equivalent to the Markovian character of the process (Prob. 2.4).

2.2.2 Master equation

Our goal is to construct an equation of motion for the single-time probability distribution $P_1(x,t)$. To this end, we begin with the identity

$$P_1(x,t') = \int dx'\, P_2(x',t;x,t') = \int dx'\, P_{1|1}(x,t'|x',t)\, P_1(x',t)\ . \tag{2.62}$$

Setting $t' = t+\tau$, we may now take the continuous-time limit:[3]

$$\begin{aligned}\frac{\partial P_1(x,t)}{\partial t} &= \lim_{\tau\to 0}\frac{P_1(x,t+\tau)-P_1(x,t)}{\tau} \\ &= \int dx'\, P_1(x',t)\lim_{\tau\to 0}\frac{P_{1|1}(x,t+\tau|x',t)-P_{1|1}(x,t|x',t)}{\tau}\ .\end{aligned} \tag{2.63}$$

For $\tau = 0$, naturally $P_{1|1}(x,t|x',t) = \delta(x-x')$, which indeed solves (2.62) for $t = t'$. To first order in τ, we try the ansatz $P_{1|1}(x,t+\tau|x',t) = A(\tau)\delta(x-x') + \tau\, W(x'\to x,t)$, where $W(x'\to x,t)$ represents the *transition rate* from the random variable value x' to x, which we henceforth also interpret as states or configurations of a physical system, during the time interval $[t,t+\tau]$. From the normalization of $P_{1|1}$ we infer $1 = A(\tau) + \tau\int dx\, W(x'\to x,t) + O(\tau^2)$, whence to order τ:

$$P_{1|1}(x,t+\tau|x',t) = \left[1-\tau\int d\bar{x}\, W(x'\to\bar{x},t)\right]\delta(x-x') + \tau\, W(x'\to x,t)\ . \tag{2.64}$$

Inserting into Eq. (2.63), and renaming integration variables, we finally obtain the *master equation*

$$\frac{\partial P_1(x,t)}{\partial t} = \int dx'\left[P_1(x',t)\, W(x'\to x,t) - P_1(x,t)\, W(x\to x',t)\right]\ . \tag{2.65}$$

This fundamental temporal evolution equation balances *gain* and *loss* terms for $P_1(x,t)$ owing to transitions from and to other states $x' \neq x$, respectively. While the master equation (2.65) is valid for any stochastic process in the continuous-time limit, a complete characterization of the kinetics requires full knowledge of the generally time- and implicitly history-dependent transition rates $W(x\to x',t)$.

Clearly, both positivity and normalization of $P_1(x,t)$ are preserved under

[3] Notice that we have defined the time derivative via *forward* discretization here; we shall follow this convention throughout this book.

the time evolution (2.65); e.g.,

$$\frac{\partial}{\partial t}\int dx\, P_1(x,t) = \int dx \int dx' \left[P_1(x',t)\, W(x' \to x,t) - P_1(x,t)\, W(x \to x',t)\right] = 0 \tag{2.66}$$

after exchanging integration variables in the second term. We may then define the associated time-dependent *entropy* as

$$S(t) = -k_{\rm B}\Big\langle \ln P_1(x,t)\Big\rangle = -k_{\rm B}\int dx\, P_1(x,t)\, \ln P_1(x,t)\ , \tag{2.67}$$

and obtain for its temporal evolution

$$\begin{aligned}\frac{\partial S(t)}{\partial t} &= -k_{\rm B}\int dx \left[\ln P_1(x,t) + 1\right]\frac{\partial P_1(x,t)}{\partial t} \\ &= \frac{k_{\rm B}}{2}\int dx\int dx' \left[P_1(x,t)W(x\to x',t) - P_1(x',t)W(x'\to x,t)\right] \\ &\qquad \times \ln\frac{P_1(x,t)}{P_1(x',t)} = \sigma(t) - \langle J_S(x,t)\rangle\ .\end{aligned} \tag{2.68}$$

The expression in the second line follows after using Eq. (2.65) and symmetrizing. Eq. (2.68) introduces the net *entropy flux* to configuration x as the average of

$$J_S(x,t) = k_{\rm B}\int dx'\, W(x\to x',t)\, \ln\frac{W(x\to x',t)}{W(x'\to x,t)}\ , \tag{2.69}$$

and the non-negative *entropy production rate*

$$\begin{aligned}\sigma(t) = \frac{k_{\rm B}}{2}\int dx\int dx' \left[P_1(x,t)\, W(x\to x',t) - P_1(x',t)\, W(x'\to x,t)\right] \\ \times \ln\frac{P_1(x,t)\, W(x\to x',t)}{P_1(x',t)\, W(x'\to x,t)} \geq 0\ ,\end{aligned} \tag{2.70}$$

where the final inequality is a consequence of the convexity of the logarithm function: $(x - x')(\ln x - \ln x') \geq 0$.

In the special case of *time-independent* transition rates, $\partial W(x \to x')/\partial t = 0$, one can show that there exists at least one *stationary solution* $P_{\rm st}(x)$ with $\partial P_{\rm st}(x)/\partial t = 0$ (provided x is confined to a finite interval). Moreover, if $P_{\rm st}(x)$ is unique, it is also stable and $\lim_{t\to\infty} P_1(x,t) = P_{\rm st}(x)$. A *sufficient* condition for the existence of such a stable stationary state can be read off from the master equation (2.65), as well as Eqs. (2.68) and (2.70): Namely, the 'in' and 'out' terms precisely balance each other for all pairs of states x, x', provided the transition rates fulfill the *detailed balance* relation

$$P_{\rm st}(x')\, W(x'\to x) = P_{\rm st}(x)\, W(x\to x')\ . \tag{2.71}$$

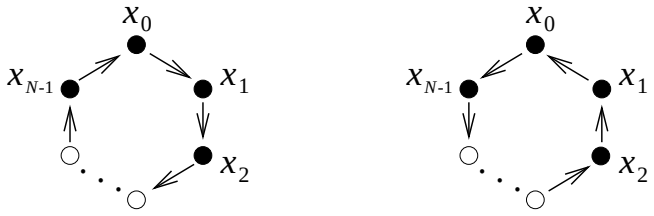

Fig. 2.4. Kolmogorov's condition for the existence of a detailed balance solution: For *any* cycle, the products of forward and backward transition rates must be equal.

Notice that $\sigma(t) = 0$ if and only if (2.71) holds: The approach to the stationary solution $P_{\rm st}(x)$ represents an *irreversible* process which terminates when $P_1(x,t) = P_{\rm st}(x)$ for all states x. Yet in order to check the detailed balance requirement (2.71), one already needs to know the stationary distribution $P_{\rm st}(x)$. A criterion based on the complete set of transition rates only is obviously preferable. In fact, a necessary and sufficient condition for the existence of a detailed balance solution to the master equation (2.65) is that for *all* possible cycles of arbitrary length N (Fig. 2.4), with not necessarily distinct intermediate states $\{x_i\}$, the forward and backward processes be equally likely (*Kolmogorov criterion*),

$$\begin{aligned} &W(x_0 \to x_1)\, W(x_1 \to x_2) \ldots W(x_{N-1} \to x_0) \\ &\quad = W(x_0 \to x_{N-1}) \ldots W(x_2 \to x_1)\, W(x_1 \to x_0)\ . \end{aligned} \tag{2.72}$$

Markov processes are fully characterized by $P_1(x,t)$ and the transition probability $P_{1|1}(x',t'|x,t)$. Inserting (2.64) with $t' = t+\tau$ into the Chapman–Kolmogorov equation (2.61) with initial state x_0 at time t_0 yields

$$\begin{aligned} \frac{\partial P_{1|1}(x,t|x_0,t_0)}{\partial t} = \int dx' \Big[&P_{1|1}(x',t|x_0,t_0)\, W(x' \to x,t) \\ &- P_{1|1}(x,t|x_0,t_0)\, W(x \to x',t) \Big] \end{aligned} \tag{2.73}$$

(Prob. 2.5). Hence, for Markov processes, both $P_1(x,t)$ and $P_{1|1}(x,t|x_0,t_0)$ obey an identical master equation, which therefore provides a *complete* description of the stochastic dynamics.

In the case of a *finite* number of discrete random variables $\{n\}$, the master equation (2.65) can be written in matrix form,

$$\begin{aligned} \frac{\partial P_n(t)}{\partial t} &= \sum_{n'} \Big[P_{n'}(t)\, W_{n' \to n}(t) - P_n(t)\, W_{n \to n'}(t) \Big] \\ &= -\sum_{n'} L_{nn'}(t)\, P_{n'}(t)\ . \end{aligned} \tag{2.74}$$

If we collect the configuration probabilities $P_n(t)$ in a *state vector* $|P(t)\rangle$, this reads in compact notation akin to an 'imaginary-time' Schrödinger equation

$$\frac{\partial}{\partial t}\,|P(t)\rangle = -\mathcal{L}(t)\,|P(t)\rangle\ , \tag{2.75}$$

where the *Liouville operator* $\mathcal{L}(t)$, which generates the temporal evolution, has the matrix elements

$$L_{nn'}(t) = -W_{n'\to n}(t) + \delta_{nn'}\sum_{\bar{n}} W_{n\to\bar{n}}(t)\ . \tag{2.76}$$

Notice that $\sum_n L_{nn'}(t) = 0$, i.e., summing over the matrix elements of $\mathcal{L}(t)$ in each column must yield zero. According to Eq. (2.74), this simply expresses total probability conservation, $\sum_n P_n(t) = 1$ for all t. Formally, this can be written as the inner product $\langle 1|P(t)\rangle = 1$ of the *projection state* vector $\langle 1| = (1, 1, \ldots, 1)$ with $|P(t)\rangle$. Upon integrating Eq. (2.75) over an infinitesimal time step, we see again that conservation of probability implies $\langle 1|\mathcal{L}(t) = \sum_n L_{nn'}(t) = 0$.

When the transition rates and thus $\mathcal{L}$ are time-independent, Eq. (2.75) is formally solved by

$$|P(t)\rangle = e^{-\mathcal{L}t}\,|P(0)\rangle\ . \tag{2.77}$$

This simply reflects that (2.74) represents a set of coupled first-order linear differential equations with constant coefficients. The ansatz $P_n(t) = e^{-\lambda t}\,\varphi_n$ then leads to an eigenvalue problem $\mathcal{L}|\alpha\rangle = \lambda^{(\alpha)}|\alpha\rangle$, or explicitly

$$\sum_{n'} L_{nn'}\,\varphi^{(\alpha)}_{n'} = \lambda^{(\alpha)}\varphi^{(\alpha)}_n\ . \tag{2.78}$$

But as in general the real matrix $L_{nn'}$ is not symmetric, these right eigenvectors differ from the left eigenvectors, which are determined as the solutions of $\langle\beta|\mathcal{L} = \lambda^{(\beta)}\langle\beta|$, i.e.,

$$\sum_{n'} \psi^{(\beta)}_{n'} L_{n'n} = \lambda^{(\beta)}\psi^{(\beta)}_n\ . \tag{2.79}$$

The eigenvectors form a bi-orthonormal set, $\langle\beta|\alpha\rangle = \sum_n \psi^{(\beta)}_n\varphi^{(\alpha)}_n = \delta^{\alpha\beta}$, and the matrix elements (2.76) may be written as $L_{nn'} = \sum_\alpha \lambda^{(\alpha)}\varphi^{(\alpha)}_n\psi^{(\alpha)}_{n'}$. The eigenvalues $\lambda^{(\alpha)}$ of the Liouville operator generally come in *complex*-conjugate pairs with $\mathrm{Re}\,\lambda^{(\alpha)} \geq 0$, and determine the oscillatory and relaxational behavior of the general solution to Eq. (2.74),

$$P_n(t) = \sum_\alpha c^{(\alpha)} e^{-\lambda^{(\alpha)}t}\varphi^{(\alpha)}_n\ . \tag{2.80}$$

Since $\langle 1|\mathcal{L}(t) = 0$, there is always at least one left eigenstate with eigenvalue 0, representing the stationary state.

If *detailed balance* holds, i.e., $P_{n'} W_{n' \to n} = P_n W_{n \to n'}$ with the stationary solution $P_n = \lim_{t\to\infty} P_n(t)$, the time evolution matrix may be symmetrized,

$$\widetilde{L}_{nn'} = \widetilde{L}_{n'n} = \begin{cases} \sum_{\bar{n}} W_{n\to\bar{n}} & n = n' \\ -W_{n'\to n}\sqrt{P_{n'}/P_n} = -W_{n\to n'}\sqrt{P_n/P_{n'}} & n \neq n' \end{cases} . \tag{2.81}$$

For $\phi_n^{(\alpha)} = \varphi_n^{(\alpha)}/\sqrt{P_n} = \psi_n^{(\alpha)}\sqrt{P_n}$, both Eqs. (2.78) and (2.79) read

$$\sum_{n'} \widetilde{L}_{nn'} \phi_{n'}^{(\alpha)} = \lambda^{(\alpha)} \phi_n^{(\alpha)} , \tag{2.82}$$

with *real*, positive eigenvalues $\lambda^{(\alpha)} \geq 0$. The lowest non-zero eigenvalue λ_m clearly dominates at sufficiently long times, when $P_n(t)$ relaxes towards the stationary solution, namely the eigenstate with zero eigenvalue.

We can construct P_{n_N} explicitly from any starting state P_{n_0} through a sequence of intermediate states with non-vanishing transition rates,

$$P_{n_N} = P_{n_{N-1}} \frac{W_{n_{N-1}\to n_N}}{W_{n_N \to n_{N-1}}} = \ldots = P_{n_0} \prod_{j=0}^{N-1} \frac{W_{n_j \to n_{j+1}}}{W_{n_{j+1}\to n_j}} .$$

Exploiting the condition (2.72), this becomes

$$P_{n_N} = P_{n_0} \frac{W_{n_0 \to n_N}}{W_{n_N \to n_0}} , \tag{2.83}$$

independent of the actual path $n_0 \to \ldots \to n_N$. One may then introduce a *potential* function Φ_n via

$$P_n = \frac{1}{Z} e^{-\Phi_n} , \quad Z = \sum_n e^{-\Phi_n} , \tag{2.84}$$

and Eq. (2.83) becomes

$$\Phi_{n_N} - \Phi_{n_0} = \sum_{j=0}^{N-1} \ln \frac{W_{n_{j+1}\to n_j}}{W_{n_j \to n_{j+1}}} = \ln \frac{W_{n_N \to n_0}}{W_{n_0 \to n_N}} . \tag{2.85}$$

We may identify the potential with an effective Hamiltonian (with energy measured in units of some fixed temperature $k_B T$), and Z with the associated canonical partition function. Thus, a stochastic process satisfying the detailed-balance condition may be viewed as describing a physical system relaxing towards thermal equilibrium. However, when the transition rates violate Eq. (2.72), there exists a non-vanishing probability current between the different configurations, and the system is inherently out of equilibrium.

In the *micro-canonical* equilibrium ensemble, the system is held at fixed total energy. But for all accessible microstates x on the energy shell *micro-reversibility* should hold, i.e., $W(x \to x') = W(x' \to x)$, compare Fermi's golden rule (2.44). The detailed-balance condition (2.71) then implies $P_{\rm st}(x) = P_{\rm st}(x')$, i.e., in thermal equilibrium the system will be found with equal probability in any of the microstates compatible with the fixed total energy constraint. In the *canonical* ensemble, the physical system described by a Hamiltonian $H(x)$ is in thermal contact with a heat bath, which provides a constant temperature T. The associated stationary probabilities are given by the canonical distribution (Boltzmann factors),

$$P_{\rm st}(x) = \frac{1}{Z(T)}\, e^{-H(x)/k_{\rm B}T} \ . \tag{2.86}$$

Transition rates satisfying detailed balance must hence obey the condition

$$\frac{W(x \to x')}{W(x' \to x)} = e^{-[H(x')-H(x)]/k_{\rm B}T} \ . \tag{2.87}$$

This is actually the microscopic kinetic background for the relation (2.11) between the absorptive and emissive branch of dynamic correlation functions, which led to the fluctuation-dissipation theorem (2.34).

A Monte Carlo computer simulation may be interpreted as a numerical solution of a master equation. One first defines the possible states of a system, e.g., for each site on a discrete lattice. Next certain rules, corresponding to the transition rates, are established according to which the configurations evolve. In order to measure physical quantities and correlations, one performs ensemble averages, over many runs, and/or temporal averages. In the master equation language, this information is encoded in the probabilities $P_1(x,t)$. If one wants to ensure that the simulation eventually reaches a stationary state such that equilibrium properties can be accessed, the assigned transition rates should satisfy detailed balance. For example, the widely employed *Metropolis algorithm* uses the rates (in units of computer time)

$$W(x \to x') = \min\left(1, e^{-[H(x')-H(x)]/k_{\rm B}T}\right) \ . \tag{2.88}$$

The move from configuration x to x' is always performed if the associated energy decreases, while such an update is done with a finite probability when $H(x') > H(x)$, i.e., is exponentially suppressed for large energy differences.

2.2.3 Kramers–Moyal expansion, Fokker–Planck equation

In the following, we assume that the possible values of the random variables x (characterizing a physical configuration) are in a continuous set. With

$x' = x - \xi$ and $t' = t + \tau$, Eq. (2.62) becomes

$$P_1(x, t+\tau) = \int d\xi \, P_{1|1}(x, t+\tau | x-\xi, t) \, P_1(x-\xi, t) \; . \tag{2.89}$$

Next, provided the transition probabilities from $x - \xi$ to x are invariant with respect to time translations, and therefore $P_{1|1}(x, t+\tau|x-\xi, t) = P_{\rm tr}(x-\xi, \xi, \tau)$ does not depend on the initial time t, we may expand with respect to the small increment ξ:

$$P_1(x, t+\tau) = \int d\xi \left(P_{\rm tr}(x, \xi, \tau) \, P_1(x, t) - \xi \, \frac{\partial}{\partial x} \Big[P_{\rm tr}(x, \xi, \tau) \, P_1(x, t) \Big] \right.$$
$$\left. + \ldots + \frac{(-\xi)^k}{k!} \, \frac{\partial^k}{\partial x^k} \Big[P_{\rm tr}(x, \xi, \tau) \, P_1(x, t) \Big] + \ldots \right) .$$

Upon defining the following limit for the kth increment moment of the transition probability,

$$\alpha_k(x) = \lim_{\tau \to 0} \frac{1}{\tau} \int d\xi \, \xi^k P_{\rm tr}(x, \xi, \tau) \; , \tag{2.90}$$

and noticing that $\int d\xi \, P_{\rm tr}(x, \xi, \tau) = 1$, we arrive at the *Kramers–Moyal expansion*

$$\frac{\partial P_1(x,t)}{\partial t} = \lim_{\tau \to 0} \frac{P_1(x, t+\tau) - P_1(x,t)}{\tau}$$
$$= \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \, \frac{\partial^k}{\partial x^k} \Big[\alpha_k(x) \, P_1(x,t) \Big] \; . \tag{2.91}$$

Specifically for Markov processes, starting from the Chapman–Kolmogorov equation (2.61) and following the same procedure one readily derives a Kramers–Moyal expansion for the transition probability $P_{1|1}(x, t|x_0, t_0)$ itself (Prob. 2.5).

In many instances, only the first two moments contribute to the formal expansion (2.91), and the remaining Kramers–Moyal coefficients vanish: Whereas $\int d\xi \, \xi \, P_{\rm tr}(x, \xi, \tau) = \tau \, \alpha_1(x)$ and $\int d\xi \, \xi^2 \, P_{\rm tr}(x, \xi, \tau) = \tau \, \alpha_2(x)$, in this case $\int d\xi \, \xi^k \, P_{\rm tr}(x, \xi, \tau) = O(\tau^2)$, whence $\alpha_k = 0$ for $k \geq 3$. Eq. (2.91) then reduces to the *Fokker–Planck equation*

$$\frac{\partial P_1(x,t)}{\partial t} = - \, \frac{\partial J_1(x,t)}{\partial x} = - \, \frac{\partial}{\partial x} \Big[\alpha_1(x) \, P_1(x,t) \Big] + \frac{1}{2} \, \frac{\partial^2}{\partial x^2} \Big[\alpha_2(x) \, P_1(x,t) \Big] \; , \tag{2.92}$$

which has the form of a continuity equation for the probability density $P_1(x,t)$, with the *probability current*

$$J_1(x,t) = \alpha_1(x) \, P_1(x,t) - \frac{1}{2} \, \frac{\partial}{\partial x} \Big[\alpha_2(x) \, P_1(x,t) \Big] \; . \tag{2.93}$$

If the random variable x is a vector quantity, i.e., more than one label is required to characterize the configuration, $\partial/\partial x$ is of course to be interpreted as the divergence operation. The Kramers–Moyal coefficient $\alpha_1(x)$ then becomes a vector as well, and $\alpha_2(x)$ a matrix (second-rank tensor). The first and second contributions on the right-hand side of (2.92) are referred to as the *drift* and *diffusion* terms, respectively (see also Sec. 2.3.1).

In fact, *Pawula's theorem* states that for non-vanishing transition probabilities $P_{\rm tr}(x,\xi,\tau) > 0$, the Kramers–Moyal expansion (2.91) may either terminate after the first or second term, which then yields the Fokker–Planck equation (2.92), or must contain *infinitely* many terms. In order to prove this remarkable statement, we introduce the scalar product $(f|g) = \int d\xi\, f(\xi) g(\xi)\, P_{\rm tr}(x,\xi,\tau)$, and exploit the associated generalized Schwarz inequality $(f|g)^2 \leq (f|f)\,(g|g)$, i.e.,

$$\left[\int d\xi\, f(\xi) g(\xi)\, P_{\rm tr}(x,\xi,\tau)\right]^2 \leq \int d\xi\, f(\xi)^2\, P_{\rm tr}(x,\xi,\tau) \times \int d\xi\, g(\xi)^2\, P_{\rm tr}(x,\xi,\tau)\ . \qquad (2.94)$$

We assume $\alpha_k \neq 0$, but all $\alpha_{k'} = 0$ for $k' > k$, and lead this assertion to contradictions for $k > 2$. For k odd, we set $f(\xi) = \xi^{(k+1)/2}$ and $g(\xi) = \xi^{(k-1)/2}$. Inserting into the inequality (2.94), dividing with τ^2, and taking $\tau \to 0$, we obtain for $k \geq 3$: $0 < \alpha_k(x)^2 \leq \alpha_{k+1}(x)\,\alpha_{k-1}(x)$. But then $\alpha_{k+1} = 0$ would imply $\alpha_k = 0$ as well, which contradicts our assumption. Yet for $k = 1$, we find instead $\tau\,\alpha_1(x)^2 \leq \alpha_2(x) = 0$, perfectly compatible with the limit $\tau \to 0$. For even k, on the other hand, the choices $f(\xi) = \xi^{(k+2)/2}$ and $g(\xi) = \xi^{(k-2)/2}$ similarly leads to $0 < \alpha_k(x)^2 \leq \alpha_{k+2}(x)\,\alpha_{k-2}(x) = 0$ for $k \geq 4$, while for $k = 2$ merely $\tau\,\alpha_2(x)^2 \leq \alpha_4(x)$. If the Kramers–Moyal expansion does not terminate at $k = 2$, we observe that certainly all even coefficients $\alpha_{2k} \neq 0$, whereas some of the odd ones might vanish.

2.3 Three examples

This concludes our brief exposition of stochastic processes. In this section, we discuss three hopefully instructive examples. Aside from providing interesting physical applications and illustrations for the general concepts introduced in Sec. 2.2, the important systems to be explored here closely relate to the non-equilibrium chapters on driven diffusive (Chap. 11) and reaction-diffusion systems (Chap. 9), and to the three subsequent chapters on equilibrium critical dynamics.

2.3.1 One-dimensional random walk and biased diffusion

As a first example, we consider a random walk on a one-dimensional chain consisting of N discrete lattice sites j, with lattice constant a_0. The possible configurations of the system can be labeled by the walker's position $x_j = ja_0$ at time t. After each time step of duration τ, the particle may either hop to the right, with probability $0 \leq p \leq 1$, or to the left, with probability $1-p$. The corresponding Markovian stochastic process is then defined by specifying the non-vanishing time-independent transition rates. For $2 \leq j \leq N-1$, we have $W_{j\to j+1} = p/\tau$ and $W_{j\to j-1} = (1-p)/\tau$. At this point, we need to specify the boundary conditions at the chain ends. For *periodic* boundary conditions, upon identifying the sites $N+1$ with 1 and 0 with N, these rules can simply be maintained for $j = N$ and $j = 1$. In the case of *reflecting* boundary conditions, we set $W_{1\to 2} = p/\tau$, and $W_{N\to N-1} = (1-p)/\tau$, while allowing no other transitions from sites 1 and N. The associated master equation reads

$$\frac{\partial P_j(t)}{\partial t} = \frac{1}{\tau}\Big[pP_{j-1}(t) - P_j(t) + (1-p)P_{j+1}(t)\Big]\,, \tag{2.95}$$

valid for all sites for periodic boundary conditions but only for $2 \leq j \leq N-1$ for an open chain, in which case we must supplement Eqs. (2.95) with

$$\begin{aligned}\frac{\partial P_1(t)}{\partial t} &= \frac{1}{\tau}\Big[-pP_1(t) + (1-p)P_2(t)\Big]\,,\\ \frac{\partial P_N(t)}{\partial t} &= \frac{1}{\tau}\Big[pP_{N-1}(t) - (1-p)P_N(t)\Big]\,.\end{aligned} \tag{2.96}$$

The choice of boundary conditions turns out to be crucial if we seek stationary solutions P_j to (2.95) that satisfy detailed balance, i.e.,

$$p\,P_j = (1-p)\,P_{j+1} \tag{2.97}$$

for all sites j and either set of boundary conditions. For the closed chain, a detailed-balance solution thus exists *only* in the unbiased case with $p = 1/2$, when obviously $P_j = 1/N$, and independent random walkers become uniformly distributed as $t \to \infty$. Indeed, Kolmogorov's criterion (2.72) is clearly violated for a biased random walk with $p \neq 1/2$ if we choose the cycle to be the entire system: $p^N \neq (1-p)^N$. The system is therefore genuinely out of equilibrium, and in the stationary state, a macroscopic particle current runs through the ring. In fact, the simple uniform probability distribution $P_j = 1/N$ satisfies Eq. (2.95). Yet for a proper characterization of this non-equilibrium stochastic process one must also specify the uniform current $\propto (2p-1)a_0/\tau$.

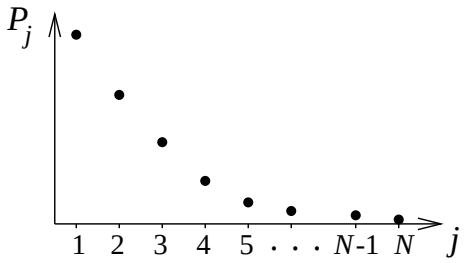

Fig. 2.5. Sketch of the stationary probability distribution for a one-dimensional biased random walk with $0 < p < 1/2$ and reflecting boundary conditions.

In the case of *reflecting* boundary conditions, on the other hand, the normalization $1 = \sum_{j=1}^{N} P_j = P_1 \sum_{j=0}^{N-1} [p/(1-p)]^j$ fixes (for $p \neq 1/2$)

$$P_1 = \frac{1-2p}{(1-p)\,[1-p^N/(1-p)^N]} \ , \tag{2.98}$$

and thence all other $P_j = [p/(1-p)]^{j-1} P_1$ through the geometric progression (2.97). This yields a stationary probability distribution that in the continuum limit, corresponds to a barometric height formula for the particle density, as shown in Fig. 2.5. In the fully directed limit with $p = 0$ one finds $P_1 = 1$, $P_j = 0$ for $2 \leq j \leq N$; as expected, the particles then accumulate at the left boundary. In the unbiased case $p = 1/2$, we again recover the flat distribution $P_j = 1/N$. In equilibrium statistical mechanics language, these two extreme cases correspond, for a fixed bias potential $U > 0$, to zero and infinite temperature, respectively: $p = 1/(1 + e^{U/k_{\rm B}T})$.

In order to take the *continuum limit*, we rewrite Eq. (2.95)

$$\frac{\partial P_j(t)}{\partial t} = \frac{1-2p}{2\tau}\Big[P_{j+1}(t) - P_{j-1}(t)\Big] + \frac{1}{2\tau}\Big[P_{j+1}(t) - 2P_j(t) + P_{j-1}(t)\Big] \ , \tag{2.99}$$

neglecting the boundaries. With $x_j = j a_0$, and letting the lattice constant $a_0 \to 0$, we have $P_j(t) \to P_1(x,t)$, and the two terms in square brackets become $2a_0\, \partial P_1(x,t)/\partial x$ and $a_0^2\, \partial^2 P_1(x,t)/\partial x^2$. Thus we directly obtain the Fokker–Planck equation, which takes the form of a *drift-diffusion* equation:

$$\frac{\partial P_1(x,t)}{\partial t} = -v\, \frac{\partial P_1(x,t)}{\partial x} + D\, \frac{\partial^2 P_1(x,t)}{\partial x^2} \ , \tag{2.100}$$

and we may identify the constant Kramers–Moyal coefficients with the *drift velocity* and *diffusion constant*,

$$v = \frac{2a_0}{\tau}\left(p - \frac{1}{2}\right) \ , \quad D = \frac{a_0^2}{2\tau} \ . \tag{2.101}$$

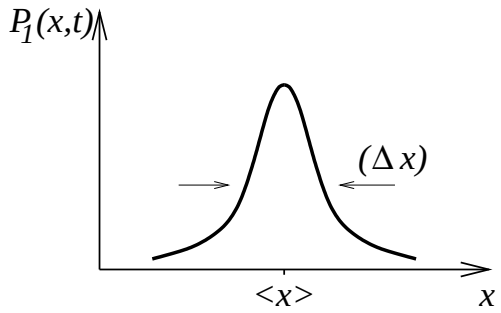

Fig. 2.6. Sketch of the solution (2.104) to the continuum drift-diffusion equation.

For this Markov process, an identical Fokker–Planck equation holds for the transition probabilities $P_{1|1}(x,t|x_0,0)$.

We proceed to solve the partial differential equation (2.100) for an infinite chain $L = (N-1)a_0 \to \infty$, and initial particle location $x_0 = 0$: $P_1(x, t=0) = \delta(x)$ (which is also the proper initial condition for the transition probability). A Galilean transformation $P_1(x,t) = G(x - vt, t)$ eliminates the drift term, and the resulting pure diffusion equation for $G(x,t)$ reads in Fourier space

$$\frac{\partial G(q,t)}{\partial t} = -Dq^2\, G(q,t) + \delta(t) \tag{2.102}$$

for $t \geq 0$, since $G(q=0,t) = \Theta(t)$. Its solution is just the diffusion *Green function*

$$G(q,t) = e^{-Dq^2 t}\, \Theta(t)\ . \tag{2.103}$$

In coordinate space, this is a Gaussian as well, and we obtain at last

$$P_1(x,t) = G(x-vt,t) = \frac{1}{\sqrt{4\pi Dt}}\, e^{-(x-vt)^2/4Dt}\, \Theta(t)\ , \tag{2.104}$$

see Fig. 2.6. Its first moments are $\langle x \rangle = vt$ and $(\Delta x)^2 = \langle x(t)^2 \rangle - \langle x \rangle^2 = 2Dt$, which is *Fick's diffusion law* for the mean-square displacement. Since the random hopping process is Markovian, the transition probability satisfies the Fokker–Planck equation (2.100) as well. All higher moments factorize for the ensuing Gaussian distribution (2.104), and are therefore at least of order t^2, which confirms that the Kramers–Moyal expansion indeed terminates after the second term. Finally, with the aid of the Green function (2.104), the solution for any arbitrary initial distribution $P_1(x,0)$ can be constructed:

$$P_1(x,t) = \int dx'\, G(x - x' - vt, t)\, P_1(x',0)\ , \tag{2.105}$$

which of course is just Eq. (2.89), since we may identify $G(x - x' - vt, t) = P_{1|1}(x, t|x', 0)$.

2.3.2 Population dynamics

Our second example represents a very simplified zero-dimensional model for population dynamics that is devoid of any spatial structure. The possible configurations are indicated by the integer number n of particles or individuals A in a population present at time t. Let us consider offspring production $A \to A + A$, with rate σ, and spontaneous death, $A \to \emptyset$, with rate κ, which both constitute 'first-order' reactions. The ensuing Markovian dynamics is implemented by defining the corresponding transition rates for the branching and decay processes, namely $W_{n\to n+1} = \sigma\, n$ and $W_{n\to n-1} = \kappa\, n$, both of which are proportional to the population number. Notice that the configuration $n = 0$ represents an *absorbing state* in the following sense: Once reached, the stochastic process stops there, and there are no fluctuations that allow the system to leave this empty configuration. Quite obviously then, detailed balance cannot be satisfied, and we are dealing with a genuine non-equilibrium system. The corresponding master equations for the time-dependent probabilities $P_n(t)$ are readily written down:

$$\frac{\partial P_n(t)}{\partial t} = \sigma(n-1)P_{n-1}(t) - (\sigma+\kappa)nP_n(t) + \kappa(n+1)P_{n+1}(t)\ . \quad (2.106)$$

In order to solve the coupled set of (infinitely many) differential equations (2.106), we introduce the *generating function*

$$g(x,t) = \sum_{n=0}^{\infty} x^n P_n(t)\ . \quad (2.107)$$

The desired probabilities $P_n(t)$ are just the nth Taylor coefficients of $g(x, t)$ in the auxiliary variable x. For example, the probability for reaching the empty, absorbing state at time t is $P_0(t) = g(0, t)$, whence the *survival probability* becomes

$$P_a(t) = 1 - g(0,t)\ . \quad (2.108)$$

Furthermore, averages are given by appropriate derivatives of $g(x, t)$, e.g., the mean population size is

$$\langle n(t)\rangle = \sum_{n=1}^{\infty} nP_n(t) = \left.\frac{\partial g(x,t)}{\partial x}\right|_{x=1}\ , \quad (2.109)$$

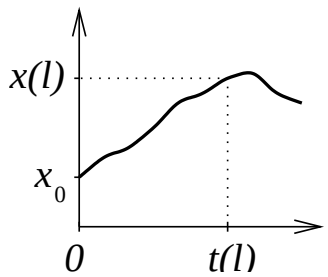

Fig. 2.7. Method of characteristics: The goal is to find a curve parametrization $x(l), t(l)$ such that $x(0) = x_0$, $t(0) = 0$, and $dg/dl = 0$.

and

$$\langle n(t)^2 \rangle = \sum_{n=1}^{\infty} n^2 P_n(t) = \frac{\partial}{\partial x} \left(x \, \frac{\partial g(x,t)}{\partial x} \right) \Big|_{x=1}$$
$$= \frac{\partial g(x,t)}{\partial x} \Big|_{x=1} + \frac{\partial^2 g(x,t)}{\partial x^2} \Big|_{x=1} , \tag{2.110}$$

etc. In addition, if initially there are n_0 particles present, i.e., $P_n(t=0) = \delta_{nn_0}$, the generating function satisfies $g(x,0) = x^{n_0}$; normalization finally gives

$$g(1,t) = \sum_{n=0}^{\infty} P_n(t) = 1 \; . \tag{2.111}$$

The crucial point, however, is that the set of infinitely many coupled master equations (2.106) is contained in the *single* partial differential equation

$$\frac{\partial g(x,t)}{\partial t} = \sum_{n=1}^{\infty} \Big[\sigma x^{n+1} - (\sigma + \kappa) x^n + \kappa x^{n-1} \Big] n P_n(t)$$
$$= \kappa (1-x) \left(1 - \frac{\sigma}{\kappa} \, x \right) \frac{\partial g(x,t)}{\partial x} \; , \tag{2.112}$$

subject to the boundary condition (2.111). In order to solve (2.112), we employ the *method of characteristics*. The idea is to view the solution as a curve in (x,t) space (Fig. 2.7) and find a parametrization $x(l), t(l)$ such that

$$\frac{dg\Big(x(l),t(l)\Big)}{dl} = \frac{\partial g(x,t)}{\partial x} \, \frac{dx(l)}{dl} + \frac{\partial g(x,t)}{\partial t} \, \frac{dt(l)}{dl} = 0 \; , \tag{2.113}$$

because then

$$g\Big(x(l),t(l)\Big) = g\Big(x(0) = x_0, t(0) = 0\Big) = x_0^{n_0} \tag{2.114}$$

according to the initial condition. Comparing Eqs. (2.112) and (2.113), we

see that we may simply choose time itself as the curve parameter, $t(l) = l$, which leaves us with a first-order ordinary differential equation

$$\frac{dx(t)}{dt} = -\kappa\,[1 - x(t)]\left[1 - \frac{\sigma}{\kappa}\,x(t)\right]. \tag{2.115}$$

Straightforward integration yields

$$-\kappa t = \int_{x_0}^{x(t)} \frac{dx'}{(1-x')(1-\sigma x'/\kappa)} = \frac{\kappa}{\kappa-\sigma}\,\ln\left[\frac{\kappa-\sigma x(t)}{\kappa-\sigma x_0}\,\frac{1-x_0}{1-x(t)}\right]$$

for $\sigma \neq \kappa$, whereas $-\kappa t = [1-x(t)]^{-1} - [1-x_0]^{-1}$ for equal rates $\sigma = \kappa$. Solving for $x_0(x,t)$ and inserting into (2.114) one arrives at

$$g(x,t) = x_0(x,t)^{n_0} = \left[\frac{(\kappa-\sigma x)\,e^{(\kappa-\sigma)t} - \kappa(1-x)}{(\kappa-\sigma x)\,e^{(\kappa-\sigma)t} - \sigma(1-x)}\right]^{n_0} \tag{2.116}$$

if $\sigma \neq \kappa$, and

$$g(x,t) = \left[\frac{1+(1-x)(\kappa t-1)}{1+(1-x)\kappa t}\right]^{n_0} \tag{2.117}$$

in the degenerate case $\sigma = \kappa$. It is easily checked that the solutions (2.116) and (2.117) satisfy the normalization condition (2.111).

From Eqs. (2.116) and (2.117), we obtain the extinction probability

$$P_0(t) = g(0,t) = \begin{cases} \left(\left[e^{(\kappa-\sigma)t} - 1\right] \Big/ \left[e^{(\kappa-\sigma)t} - \frac{\sigma}{\kappa}\right]\right)^{n_0} & \sigma \neq \kappa \\ \left[\kappa t/(1+\kappa t)\right]^{n_0} & \sigma = \kappa \end{cases}. \tag{2.118}$$

The extinction probability grows (decreases) exponentially in time if $\kappa > \sigma$ ($\kappa < \sigma$), with a characteristic time scale $\tau_c = 1/|\kappa - \sigma|$. As the control parameter $\kappa/\sigma \to 1$, τ_c diverges, and $P_0(t)$ initially follows a power law. In this sense, our zero-dimensional model displays features that resemble critical behavior near a continuous phase transition. As a possible order parameter, one may use the asymptotic survival probability

$$P_a = 1 - \lim_{t\to\infty} P_0(t) = \begin{cases} 1 - (\kappa/\sigma)^{n_0} & \kappa < \sigma \\ 0 & \kappa \geq \sigma \end{cases}, \tag{2.119}$$

plotted in Fig. 2.8. Lastly, we determine the mean population size using Eq. (2.109), $\langle n(t)\rangle = n_0\,e^{(\sigma-\kappa)t}$. Consequently, $n_\infty = \lim_{t\to\infty}\langle n(t)\rangle$ vanishes in the *inactive* state ($\kappa > \sigma$), diverges in the *active* phase ($\kappa < \sigma$), whereas $\langle n(t)\rangle = n_0$ precisely at the extinction threshold. A straightforward calculation (Prob. 2.6) yields that the mean-square particle number fluctuations grow linearly in time at this 'critical point': $(\Delta n)^2 = 2n_0\kappa t$. With balancing production and decay rates, the stochastic process $\{n(t)\}$ may be viewed as

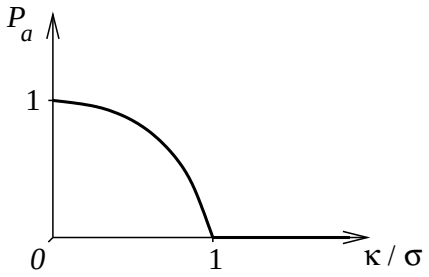

Fig. 2.8. Asymptotic survival probability for the population model as function of the ratio κ/σ of the decay and branching rates.

a one-dimensional unbiased random walk, starting at n_0, and with effective 'diffusion' constant $n_0\kappa$. We remark that if we replace the branching process with spontaneous particle creation $\emptyset \to A$ with rate $\tau > 0$, i.e., $W_{n\to n+1} = \tau$ (independent of n), the system always resides in the active state with finite particle density $n_\infty = \tau/\kappa$ (see Prob. 2.7).

2.3.3 Kinetic Ising models

As a final example, we construct *equilibrium* kinetics for the ferromagnetic Ising model (1.10). Its possible configurations are given by the set of spin values $\{\sigma_i = \pm 1\}$ at each lattice site i. We take the thermodynamic limit, and shall not worry about boundary conditions here. Starting from an arbitrary initial state, the simplest Markovian dynamics consists of allowing local *spin flips* $\sigma_i \to -\sigma_i$ with certain rates $W(\sigma_i)$. This is usually referred to as *Glauber* kinetics. In order to ensure that the system eventually relaxes to the canonical distribution, we impose detailed balance, which we may conveniently write in terms of the effective local fields (1.14) as

$$e^{h_{\mathrm{eff},i}\sigma_i/k_\mathrm{B}T}\, W(\sigma_i) = e^{-h_{\mathrm{eff},i}\sigma_i/k_\mathrm{B}T}\, W(-\sigma_i)\ . \tag{2.120}$$

As $\sigma_i^2 = 1$, we have the identity

$$e^{\pm h_{\mathrm{eff},i}\sigma_i/k_\mathrm{B}T} = \left(1 \pm \sigma_i \tanh\frac{h_{\mathrm{eff},i}}{k_\mathrm{B}T}\right)\cosh\frac{h_{\mathrm{eff},i}}{k_\mathrm{B}T}\ ,$$

and a simple choice for the transition rates that satisfies Eq. (2.120) is

$$W(\sigma_i) = \Gamma_\mathrm{G}\left(1 - \sigma_i \tanh\frac{h_{\mathrm{eff},i}}{k_\mathrm{B}T}\right) \tag{2.121}$$

with a constant flip rate Γ_G. Notice that for $T \to \infty$, the energetics becomes irrelevant, and all rates equal to Γ_G. For $T = 0$, on the other hand, $W(\sigma_i) =$

$\Gamma_{\rm G}(1-\sigma_i \,{\rm sgn}\, h_{{\rm eff},i})$: The spin at site i may only flip, with rate $2\Gamma_{\rm G}$, if the net effective field there points in the opposite direction.

In one dimension, and with nearest-neighbor exchange couplings only, $h_{{\rm eff},i} = h + J(\sigma_{i-1} + \sigma_{i+1})$, and the rates $W(\sigma_i)$ depend just on the values of the two adjacent spins. This yields the following list of possible processes and respective Glauber transition rates:

$$\begin{aligned}
\uparrow\uparrow\uparrow &\to \uparrow\downarrow\uparrow \qquad \Gamma_{\rm G}\left(1-\tanh\frac{h+2J}{k_{\rm B}T}\right)\\
\uparrow\uparrow\downarrow &\to \uparrow\downarrow\downarrow \qquad \Gamma_{\rm G}\left(1-\tanh\frac{h}{k_{\rm B}T}\right)\\
\downarrow\uparrow\uparrow &\to \downarrow\downarrow\uparrow \qquad \Gamma_{\rm G}\left(1-\tanh\frac{h}{k_{\rm B}T}\right)\\
\downarrow\uparrow\downarrow &\to \downarrow\downarrow\downarrow \qquad \Gamma_{\rm G}\left(1-\tanh\frac{h-2J}{k_{\rm B}T}\right)\\
\uparrow\downarrow\uparrow &\to \uparrow\uparrow\uparrow \qquad \Gamma_{\rm G}\left(1+\tanh\frac{h+2J}{k_{\rm B}T}\right)\\
\uparrow\downarrow\downarrow &\to \uparrow\uparrow\downarrow \qquad \Gamma_{\rm G}\left(1+\tanh\frac{h}{k_{\rm B}T}\right)\\
\downarrow\downarrow\uparrow &\to \downarrow\uparrow\uparrow \qquad \Gamma_{\rm G}\left(1+\tanh\frac{h}{k_{\rm B}T}\right)\\
\downarrow\downarrow\downarrow &\to \downarrow\uparrow\downarrow \qquad \Gamma_{\rm G}\left(1+\tanh\frac{h-2J}{k_{\rm B}T}\right) .
\end{aligned} \tag{2.122}$$

Of course, the external field h favors spin flips in its direction. For $h = 0$, this bias disappears, and the first four of the above processes become degenerate with their $\uparrow \leftrightarrow \downarrow$ 'mirror' images. We may then employ the *domain wall* representation of the Ising system, where a pair of opposite spins is labeled as a 'particle' A, while a pair of parallel spins is viewed as an empty space $\emptyset$. In this language, the four elementary Glauber processes translate to pair creation, unbiased hopping, and pair annihilation of domain walls, respectively, with the following rates:

$$\begin{aligned}
\emptyset\,\emptyset &\to A\,A \qquad \Gamma_{\rm G}\left(1-\tanh\frac{2J}{k_{\rm B}T}\right)\\
\emptyset\,A &\to A\,\emptyset \qquad \Gamma_{\rm G}\\
A\,\emptyset &\to \emptyset\,A \qquad \Gamma_{\rm G}\\
A\,A &\to \emptyset\,\emptyset \qquad \Gamma_{\rm G}\left(1+\tanh\frac{2J}{k_{\rm B}T}\right) .
\end{aligned} \tag{2.123}$$

As the temperature decreases to zero, domain wall creation is rendered impossible, and the annihilation rate becomes twice the hopping rate. The

kinetic Ising system approaches the ordered state through expelling the interfaces. Within the mean-field approximation, we may infer the overall density $n(t)$ of domain walls by means of an approximate rate equation that balances the spontaneous production and pair annihilation contributions,

$$\frac{1}{\Gamma_{\rm G}}\,\frac{dn(t)}{dt} = \left(1-\tanh\frac{2J}{k_{\rm B}T}\right)[1-n(t)]^2 - \left(1+\tanh\frac{2J}{k_{\rm B}T}\right)n(t)^2 \ . \quad (2.124)$$

In the stationary state, we thus find the domain wall density

$$n_s = \left(1+\sqrt{\frac{1+\tanh(2J/k_{\rm B}T)}{1-\tanh(2J/k_{\rm B}T)}}\,\right)^{-1} = \frac{1}{1+e^{2J/k_{\rm B}T}} \ , \quad (2.125)$$

which vanishes exponentially as $T \to 0$, proportional to the inverse correlation length (compare Prob. 1.2), whereas $n_s \to 1/2$ as $T \to \infty$.

Under Glauber kinetics, the total magnetization $M = \sum_i \sigma_i$ is not conserved. However, for the Ising model without additional anisotropies, M is actually a *conserved* quantity, its fixed value being determined by the external field h. A more appropriate microscopic relaxation mechanism therefore consists of *spin exchanges* $\sigma_i \leftrightarrow \sigma_j \neq \sigma_i$, called *Kawasaki* dynamics, with transition rates $W(\sigma_i \leftrightarrow \sigma_j) \propto \Gamma_K \frac{1}{2}(1-\sigma_i\sigma_j)$. In the lattice gas representation (1.30), this simply describes particle transfers to empty sites; h is then related to the chemical potential that fixes the overall particle number $\sum_i n_i = \frac{1}{2}(N+M)$. According to detailed balance, the exchange rates $W(\sigma_i \leftrightarrow \sigma_j)$ will again be determined by the energetics, but become independent of the external field h. In one dimension and for purely nearest-neighbor interactions, we have the following elementary processes, both in the spin and domain wall picture, and corresponding rates:

$$\begin{array}{llllll}
\uparrow\uparrow\downarrow\uparrow & \to & \uparrow\downarrow\uparrow\uparrow & \emptyset\ A\ A & \to & A\ A\ \emptyset \qquad \Gamma_{\rm K} \\
\uparrow\uparrow\downarrow\downarrow & \to & \uparrow\downarrow\uparrow\downarrow & \emptyset\ A\ \emptyset & \to & A\ A\ A \qquad \Gamma_b \\
\downarrow\uparrow\downarrow\uparrow & \to & \downarrow\downarrow\uparrow\uparrow & A\ A\ A & \to & \emptyset\ A\ \emptyset \qquad \Gamma_a \\
\downarrow\uparrow\downarrow\downarrow & \to & \downarrow\downarrow\uparrow\downarrow & A\ A\ \emptyset & \to & \emptyset\ A\ A \qquad \Gamma_{\rm K}\ . \quad (2.126)
\end{array}$$

In particle language, the first and last process represent hopping, the second one branching, and the third one fusion. As $T \to \infty$, all rates must become equal, while for $T \to 0$ one should expect $\Gamma_b \to 0$ and $\Gamma_a \to 2\Gamma_{\rm K}$. In general, $\Gamma_a + \Gamma_b = 2\Gamma_{\rm K}$; in addition, the detailed balance conditions imply

$$\Gamma_b = e^{-4J/k_{\rm B}T}\,\Gamma_a \quad (2.127)$$

for the second and third of the above spin exchange processes and their

reverse, whence

$$\Gamma_a = \frac{2\Gamma_\mathrm{K}}{1+e^{-4J/k_\mathrm{B}T}} = \Gamma_\mathrm{K}\left(1+\tanh\frac{2J}{k_\mathrm{B}T}\right) ,$$
$$\Gamma_b = \frac{2\Gamma_\mathrm{K}}{1+e^{4J/k_\mathrm{B}T}} = \Gamma_\mathrm{K}\left(1-\tanh\frac{2J}{k_\mathrm{B}T}\right) . \qquad (2.128)$$

The mean-field rate equation for the average domain wall density now reads

$$\frac{1}{\Gamma_\mathrm{K}}\,\frac{dn(t)}{dt} = \left(1-\tanh\frac{2J}{k_\mathrm{B}T}\right) n(t)[1-n(t)]^2 - \left(1+\tanh\frac{2J}{k_\mathrm{B}T}\right) n(t)^3 , \qquad (2.129)$$

with the same stationary solution (2.125) as for the Glauber model.

2.4 Langevin equations

As mentioned above, solving the fully microscopic equations of motion for stochastic dynamical systems is rarely feasible. Neither is it really desired: A description in terms of a few *mesoscopic* degrees of freedom, whose averages yield macroscopic observables, is much preferable. This requires some sort of *coarse-graining*. Moreover, we are typically interested in the long-time behavior of certain characteristic quantities, and not in their complete short-time kinetics. Provided an appropriate *separation of time scales* applies, we may attempt to formulate dynamic equations for the relevant 'slow' mesoscopic degrees of freedom. The 'fast' microscopic variables then act on the former as random forces, and can be viewed as system-inherent stochastic *noise*. This leads to *Langevin* stochastic differential equations, which have proven quite useful in the study of dynamic critical phenomena, both in and away from thermal equilibrium.[4]

2.4.1 Langevin–Einstein theory of Brownian motion

We begin with a brief study of *Brownian motion*: A large, heavy particle, with mass m, moves with velocity v (a d-dimensional vector) in a fluid consisting of many small, light particles. The impacts with the fluid particles are modeled through a stochastic force $f(t)$. In addition, the random collisions on average generate a *friction* force $-m\zeta v$. Newton's equation of motion for the Brownian particle thus becomes a *stochastic differential equation*

$$m\,\frac{\partial v(t)}{\partial t} = -m\zeta\, v(t) + f(t) . \qquad (2.130)$$

[4] Good introductions to Langevin dynamics can also be found in Reif (1985), Chaikin and Lubensky (1995), Pathria (1996), Cowan (2005), Schwabl (2006), Kardar (2007), Reichl (2009), and Van Vliet (2010).

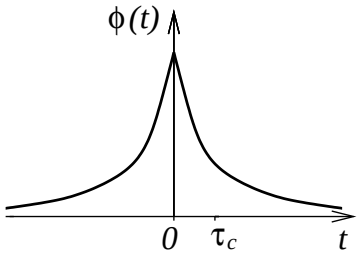

Fig. 2.9. Typical correlation function for the stochastic forces.

In order to solve the *Langevin equation* (2.130), we need to specify the statistical properties of the random force $f(t)$. As we have already taken care of the mean effect of the collisions through the friction term, the time average of the stochastic force on a given large particle, or equivalently, the ensemble average over a large set of alike Brownian particles, vanishes,

$$\langle f(t) \rangle = 0 \ . \tag{2.131}$$

For the second moment, we assume time translation invariance, and take the d spatial force components to be uncorrelated:

$$\langle f_i(t) f_j(t') \rangle = \phi(t-t') \, \delta_{ij} \ . \tag{2.132}$$

In the spirit of the central-limit theorem we demand that the specification of the first two moments (2.131) and (2.132) should suffice to fully characterize this stochastic process, which we hence presume to be *Gaussian*.

We expect the stochastic forces to lose any correlations beyond a typical time scale τ_c, roughly the duration of a collision with a fluid particle; e.g.,

$$\phi(t) = \frac{\lambda}{2\tau_c} \, e^{-|t|/\tau_c} \ . \tag{2.133}$$

In general, $\phi(t) = \phi(-t)$ is a symmetric function, with $\phi(0) = \langle f(t)^2 \rangle / d \geq 0$, and we expect $\lim_{|t-t'|\to\infty} \phi(t-t') \delta_{ij} = \langle f_i(t) \rangle \langle f_j(t') \rangle = 0$. Because of $0 \leq \langle [f(t) \pm f(t')]^2 \rangle = 2d \, [\phi(0) \pm \phi(t-t')]$, furthermore $|\phi(t)| \leq \phi(0)$; see Fig. 2.9. The Fourier transform of the memory function $\phi(t)$ is symmetric as well, $\phi(\omega) = \phi(-\omega)$, and satisfies the *Wiener–Khintchine theorem*

$$\phi(t=0) = \frac{1}{d} \left\langle f(t)^2 \right\rangle = \frac{1}{\pi} \int_0^\infty \phi(\omega) \, d\omega \ . \tag{2.134}$$

For example, the Fourier transform of Eq. (2.133) is a Lorentzian with line width $1/\tau_c$,

$$\phi(\omega) = \frac{\lambda/\tau_c^2}{\omega^2 + 1/\tau_c^2} \ . \tag{2.135}$$

If we are interested in the long-time limit $t \gg \tau_c$ only, we may effectively replace (2.133) with a delta function,

$$\phi(t) \to \lambda\,\delta(t)\ , \tag{2.136}$$

or equivalently $\phi(\omega) \to \phi(\omega = 0) = \lambda$, yielding uncorrelated *white noise*.

In this limit, the associated Gaussian probability distribution for the stochastic forces becomes

$$P[f] = C\,\exp\left[-\frac{1}{2\lambda}\int_{t_0}^{t_f} f(t)^2\,dt\right] \tag{2.137}$$

for processes starting at time t_0 and ending at t_f. Averages over random force histories may then be computed via functional integration $\langle A[f]\rangle = \int\!\mathcal{D}[f]\,A[f]\,P[f]$. The integral over all possible 'paths' $f(t)$ is constructed through temporal discretization with M time steps of length $\tau = (t_f - t_0)/M$, $t_l = t_0 + l\tau$, $l = 0, \ldots, M$, where we identify $t_M = t_f$. Upon defining the functional integration measure explicitly via

$$\mathcal{D}[f] = \lim_{\tau\to 0}\prod_{l=0}^{M-1}\left(\frac{\tau}{2\pi\lambda}\right)^{d/2} d^d f(t_l)\ , \tag{2.138}$$

we obtain

$$\int\!\mathcal{D}[f]\,P[f] = \lim_{\tau\to 0}\int\prod_{l=0}^{M-1}\left(\frac{\tau}{2\pi\lambda}\right)^{d/2} d^d f(t_l)\,\exp\left[-\frac{\tau}{2\lambda}\sum_{l=0}^{M-1} f(t_l)^2\right] = 1\ ,$$

whereupon we can set the normalization constant $C = 1$. As a check, we also compute

$$\langle f_i(t_l) f_j(t_{l'})\rangle = \lambda\,\frac{\delta_{ll'}}{\tau}\,\delta_{ij}\ ,$$

i.e., the appropriately discretized version of (2.132) and (2.136).

In order to proceed with the analysis of the Langevin equation (2.130), we apply the Green function technique. The associated differential equation $\partial G(t)/\partial t + \zeta\,G(t) = \delta(t)$ is solved by $G(t) = e^{-\zeta t}\,\Theta(t)$. With $v(t=0) = v_0$, the solution of the homogeneous part of Eq. (2.130) reads $v(t) = v_0\,e^{-\zeta t}$, whence that of the full, inhomogeneous equation becomes

$$\begin{aligned} v(t) &= v_0\,e^{-\zeta t} + \frac{1}{m}\int_0^\infty G(t-t')f(t')\,dt' \\ &= e^{-\zeta t}\left(v_0 + \frac{1}{m}\int_0^t e^{\zeta t'} f(t')\,dt'\right)\ . \end{aligned} \tag{2.139}$$

Let us now consider the velocity correlation function

$$\langle v_i(t) v_j(t')\rangle = e^{-\zeta(t+t')}\left[v_{0i}v_{0j} + \frac{\delta_{ij}}{m^2}\int_0^t d\tau\int_0^{t'} d\tau'\,e^{\zeta(\tau+\tau')}\,\phi(\tau-\tau')\right]\ ,$$

where we have inserted the moments (2.131) and (2.132). For $\tau_c \to 0$, we may use Eq. (2.136), whereupon the double integral here reduces to $\lambda(e^{2\zeta t}-1)/2\zeta$ for $t<t'$, and thus

$$\langle v_i(t)v_j(t')\rangle = \left(v_{0i}v_{0j} - \frac{\lambda}{2\zeta m^2}\,\delta_{ij}\right) e^{-\zeta(t+t')} + \frac{\lambda}{2\zeta m^2}\,\delta_{ij}\,e^{-\zeta|t-t'|}\ . \quad (2.140)$$

Asymptotically for $t,t' \gg 1/\zeta$, only the last term survives. If we assume that the Brownian particle eventually equilibrates with the fluid at temperature T, we may employ the classical equipartition theorem, $\frac{d}{2}\,k_{\rm B}T = \frac{m}{2}\,\langle v(t)^2\rangle = d\lambda/4\zeta m$, to obtain *Einstein's relation*

$$\lambda = 2\zeta m\,k_{\rm B}T\ . \quad (2.141)$$

Hence, in thermal *equilibrium*, the relaxation coefficient ζ is determined by the strength of the noise correlations λ and $k_{\rm B}T$. Notice that a *double* separation of time scales has been applied here, namely $\tau_c \ll 1/\zeta \ll t$. If we relax the first condition, we just need to replace λ with $\phi(\omega=0)$,

$$\zeta = \frac{\phi(\omega=0)}{2m\,k_{\rm B}T} = \frac{1}{2dm\,k_{\rm B}T}\int_{-\infty}^{\infty}\langle f(t)\cdot f(0)\rangle\,dt\ . \quad (2.142)$$

This relation is called the *fluctuation-dissipation theorem of the second kind*. It ensures that the kinetic energy dissipation in the Langevin equation (2.130) is on average balanced by the fluctuating force input, see Prob. 2.8, and that the system eventually relaxes to thermal equilibrium.

The Brownian particle's mean-square displacement follows from $x(t) = \int_0^t v(\tau)\,d\tau$ and our previous result (2.140):

$$\begin{aligned}\left\langle x(t)^2\right\rangle &= \int_0^t d\tau\int_0^t d\tau'\,\langle v(\tau)\cdot v(\tau')\rangle \quad (2.143)\\ &= \left(v_0^2 - \frac{d\lambda}{2\zeta m^2}\right)\left(\int_0^t e^{-\zeta\tau}\,d\tau\right)^2 + \frac{d\lambda}{2\zeta m^2}\int_0^t d\tau\int_0^t d\tau'\,e^{-\zeta|\tau-\tau'|}\\ &= \left(v_0^2 - \frac{d\lambda}{2\zeta m^2}\right)\frac{1}{\zeta^2}\left(1-e^{-\zeta t}\right)^2 + \frac{d\lambda}{\zeta^2 m^2}\left[t - \frac{1}{\zeta}\left(1-e^{-\zeta t}\right)\right]\end{aligned}$$

after straightforward integration. At short times $\tau_c \ll t \ll 1/\zeta$, a Taylor expansion to order $(\zeta t)^2$ yields *ballistic* motion with the initial velocity: $\langle x(t)^2\rangle \approx v_0^2 t^2$. For $t \gg 1/\zeta$, on the other hand, we may neglect $e^{-\zeta t}$, and the result becomes independent of the initial condition. With $\langle x(t)\rangle = v_0\,(1-e^{-\zeta t})/\zeta$, Eq. (2.143) then yields *Fick's diffusion law* $(\Delta x)^2 \approx 2Dt$, with the diffusion coefficient

$$D = \frac{d\lambda}{2\zeta^2 m^2} = \frac{d}{\zeta m}\,k_{\rm B}T\ . \quad (2.144)$$

In the last equation, we have inserted the Einstein relation (2.141).

2.4.2 Fokker–Planck equation for free Brownian motion

The solution $\{v(t)\}$ of the Langevin equation (2.130) for a free Brownian particle can be viewed as a stochastic process. For the associated Kramers–Moyal expansion, we need the moments of the velocity increments $\xi(t) = v(t+\tau) - v(t)$,

$$\alpha_{i_1 \dots i_k}(v) = \lim_{\tau \to 0} \frac{1}{\tau} \int d^d\xi \, \xi_{i_1} \dots \xi_{i_k} P_{\rm tr}(v, \xi, \tau) \ . \tag{2.145}$$

We utilize time translation invariance, and obtain from the explicit solution (2.139): $\langle v(\tau) - v_0 \rangle = (e^{-\zeta\tau} - 1)v_0 \to -\zeta\tau v_0$ as $\tau \to 0$. Hence the first Kramers–Moyal coefficient becomes $\alpha_1(v) = -\zeta v$. For the second moment, we compute with the aid of Eq. (2.140)

$$\langle [v_i(\tau) - v_{i0}][v_j(\tau) - v_{j0}] \rangle = v_{0i} v_{0j} \left(e^{-\zeta\tau} - 1 \right)^2 - \frac{\lambda}{2\zeta m^2} \, \delta_{ij} \left(e^{-2\zeta\tau} - 1 \right) \ ,$$

whence $\alpha_{ij} = \lambda \delta_{ij}/m^2$, independent of v. In order to determine the remaining moments, we use $\zeta\tau \ll 1$ right away, apply forward integration to Eq. (2.130),

$$v(t+\tau) - v(t) \approx -\zeta\tau \, v(t) + \frac{1}{m} \int_t^{t+\tau} f(t') \, dt' \ , \tag{2.146}$$

and exploit the properties of the Gaussian distribution (2.137). Thus,

$$\begin{aligned} \langle \xi_i \xi_j \xi_k \rangle \approx \, & (-\zeta\tau)^3 v_i v_j v_k \\ & -\zeta\tau \Big(v_i \delta_{jk} + v_j \delta_{ik} + v_k \delta_{ij} \Big) \int_t^{t+\tau} dt' \int_t^{t+\tau} dt'' \, \frac{\lambda}{m^2} \, \delta(t - t') \ , \end{aligned}$$

which is of order τ^2, as the double integral in the second term yields $\lambda\tau/m^2$. Similarly, we obtain

$$\begin{aligned} \langle \xi_i \xi_j \xi_k \xi_l \rangle \approx \, & (-\zeta\tau)^4 v_i v_j v_k v_l + (\zeta\tau)^2 \Big(v_i v_j \delta_{kl} + 5 \text{ permutations} \Big) \, \frac{\lambda}{m^2} \, \tau \\ & + (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \left(\frac{\lambda}{m^2} \, \tau \right)^2 \ . \end{aligned}$$

Consequently, $\alpha_{ijk}(v) = 0 = \alpha_{ijkl}(v)$, and according to Pawula's theorem, all higher Kramers–Moyal coefficients vanish as well. The probability distribution $P_1(v,t)$ for free Brownian motion therefore obeys the Fokker–Planck equation

$$\frac{\partial P_1(v,t)}{\partial t} = \zeta \, \frac{\partial}{\partial v} \cdot [v P_1(v,t)] + \frac{\lambda}{2m^2} \, \frac{\partial^2 P_1(v,t)}{\partial v^2} \ . \tag{2.147}$$

It is instructive to derive Eq. (2.147) directly from the identity

$$P_1(v,t) = \Big\langle \delta\Big(v - v(t)\Big) \Big\rangle \ . \tag{2.148}$$

Upon inserting Eq. (2.130) one finds

$$\frac{\partial P_1(v,t)}{\partial t} = -\frac{\partial}{\partial v} \cdot \Big\langle \delta\Big(v - v(t)\Big) \left[-\zeta\, v(t) + \frac{1}{m}\, f(t) \right] \Big\rangle \ .$$

In the first term, we may replace $v(t)$ with v, which yields the drift term in the Fokker–Planck equation. For the second contribution, we recall the definition of averages with the Gaussian probability distribution (2.137), and integrate by parts

$$\begin{aligned} \Big\langle \delta\Big(v - v(t)\Big) f(t) \Big\rangle &= \int \mathcal{D}[f]\, \delta\Big(v - v(t)\Big) f(t)\, \exp\left[-\frac{1}{2\lambda} \int f(t')^2\, dt' \right] \\ &= -\lambda \int \mathcal{D}[f]\, \delta\Big(v - v(t)\Big)\, \frac{\delta}{\delta f(t)}\, \exp\left[-\frac{1}{2\lambda} \int f(t')^2\, dt' \right] \\ &= \lambda \left\langle \frac{\delta}{\delta f(t)}\, \delta\Big(v - v(t)\Big) \right\rangle = -\lambda\, \frac{\partial}{\partial v} \left\langle \delta\Big(v - v(t)\Big)\, \frac{\delta v(t)}{\delta f(t)} \right\rangle . \end{aligned} \tag{2.149}$$

Lastly we obtain from the explicit solution (2.139)

$$\frac{\delta v(t)}{\delta f(t)} = \frac{e^{-\zeta t}}{m} \int_0^t e^{\zeta t'}\, \delta(t - t')\, dt' = \frac{1}{2m} \ , \tag{2.150}$$

and collecting all contributions, we are led to the diffusion term in (2.147).

Writing the Fokker–Planck equation in the form of a continuity equation as in Eq. (2.92), we find for the probability current

$$J_1(v,t) = -\zeta v P_1(v,t) - \frac{\lambda}{2m^2}\, \frac{\partial P_1(v,t)}{\partial v} \ . \tag{2.151}$$

For a stationary solution $P_{\rm st}(v)$, $J_{\rm st}(v) = 0$. Provided the Einstein relation (2.141) holds, this condition is indeed satisfied by the classical *Maxwell–Boltzmann velocity distribution*

$$P_{\rm st}(v) = \left(\frac{m}{2\pi\, k_{\rm B} T} \right)^{d/2} e^{-mv^2/2k_{\rm B}T} \ . \tag{2.152}$$

This is confirmed by an explicit solution of the Fokker–Planck equation (2.147). To this end, we substitute $\rho(v,t) = v\, e^{\zeta t}$ into $P_1(v,t) = Y(\rho,t)$, whence

$$\frac{\partial Y(\rho,t)}{\partial t} = d\zeta\, Y(\rho,t) + \frac{\lambda}{2m^2}\, e^{2\zeta t}\, \frac{\partial^2 Y(\rho,t)}{\partial \rho^2} \ .$$

The ansatz $Y(\rho,t) = X(\rho,t)\, e^{d\zeta t}$ then eliminates the homogeneous term,

leaving us with a diffusion equation with time-dependent diffusion coefficient $D(t)$. The latter is solved simply through replacing Dt in the standard results with the integral $\int_0^t D(t')\,dt'$. Here, this amounts to transforming to a new time variable $\theta(t) = (e^{2\zeta t} - 1)/2\zeta$ with $\theta(0) = 0$, which yields the normal diffusion equation

$$\frac{\partial X(\rho,\theta)}{\partial \theta} = \frac{\lambda}{2m^2}\,\frac{\partial^2 X(\rho,\theta)}{\partial \rho^2}\ .$$

Notice that with the initial condition $v(t=0) = v_0$, we have $P_1(v,t) = P_{1|1}(v,t|v_0,0)$. As we shall see below, in the case of uncorrelated noise (2.136) the Langevin equation indeed describes a Markovian stochastic process, and the transition probability satisfies the very same Fokker–Planck equation (2.147), see Prob. 2.5. For $\rho(0) = v_0$, we find with the straightforward generalization of Eq. (2.104) to d space dimensions

$$X_{1|1}\Big(\rho(v,t),\theta(t)|v_0,0\Big) = \left(\frac{m^2}{2\pi\lambda\,\theta(t)}\right)^{d/2} e^{-m^2[\rho(v,t)-v_0]^2/2\lambda\theta(t)}\ ,$$

and hence in terms of the original variables

$$P_{1|1}(v,t|v_0,0) = \left[\frac{\zeta m^2}{\pi\lambda(1-e^{-2\zeta t})}\right]^{d/2} \exp\left[-\frac{\zeta m^2 (v - v_0\,e^{-\zeta t})^2}{\lambda(1-e^{-2\zeta t})}\right]\ . \quad (2.153)$$

Initially, this becomes $P_{1|1}(v,0|v_0,0) = \delta(v-v_0)$, as it should, while asymptotically

$$P_{1|1}(v,t\to\infty|v_0,0) = P_{\rm st}(v) = \left(\frac{\zeta m^2}{\pi\lambda}\right)^{d/2} e^{-\zeta m^2 v^2/\lambda}\ , \quad (2.154)$$

independent of v_0. For $\lambda = 2\zeta m\,k_{\rm B}T$, this is exactly the Maxwell–Boltzmann distribution (2.152). Given an arbitrary normalized initial velocity distribution $w_0(v)$ with $\int w_0(v)\,d^dv = 1$, the general solution of Eq. (2.147) reads

$$P_1(v,t) = \int P_{1|1}(v,t|v',0)\,w_0(v')\,d^dv'\ , \quad (2.155)$$

see Eqs. (2.62) or (2.105), since $P_{1|1}(v,t|v_0,0)$ is just the corresponding Green function. Thus $P_1(v,0) = w_0(v)$, whereas $P_1(v,t\to\infty) = P_{\rm st}(v)$: Quite independent of the initial conditions, the probability distribution relaxes to the same stationary limit, namely Eq. (2.154).

2.4.3 Random motion in an external potential

We now generalize the above considerations to the motion of a Brownian particle in an external potential $V(x)$, as shown in Fig. 2.10. With $v(t) =$

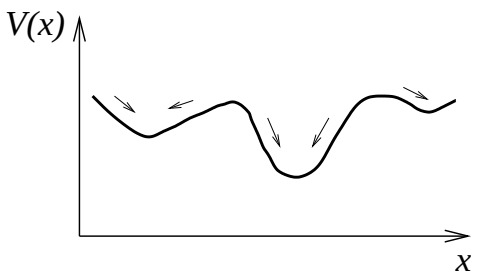

Fig. 2.10. Brownian motion in an external potential $V(x)$.

$\partial x(t)/\partial t$, and the force $F(x) = -\partial V(x)/\partial x$, Newton's equation now reads

$$m\,\frac{\partial^2 x(t)}{\partial t^2} = -m\,\zeta\,\frac{\partial x(t)}{\partial t} + F(x) + f(t)\ , \tag{2.156}$$

where we assume the same statistical properties (2.131), (2.132) for the stochastic force as before. Specifically, we may use (2.136) in the limit of short collision times, and Einstein's relation (2.141) holds in thermal equilibrium.

In the case of strong damping, where $\zeta|v| \gg |\dot{v}|$, we may neglect the inertial term. Thus we arrive at the Langevin equation in the overdamped limit,

$$\frac{\partial x(t)}{\partial t} = -\Gamma\,\frac{\partial V(x)}{\partial x} + r(t)\ , \tag{2.157}$$

where $\Gamma = 1/m\zeta$ and $r(t) = f(t)/m\zeta$, whence

$$\langle r(t)\rangle = 0\ , \quad \langle r_i(t) r_j(t')\rangle = 2\Gamma\,k_{\rm B}T\,\delta_{ij}\delta(t-t')\ , \tag{2.158}$$

with the associated Gaussian probability distribution

$$P[r] = \exp\left[-\,\frac{1}{4\Gamma\,k_{\rm B}T}\int r(t)^2\,dt\right]\ , \tag{2.159}$$

with the functional integration measure defined as in Eq. (2.138). Under purely deterministic, overdamped dynamics, the particles will accumulate in the potential minima closest to their starting positions, as indicated in Fig. 2.10. In the presence of thermal noise, the Brownian particles may escape from these local potential minima with a finite probability, and for $t \to \infty$ the equilibrium distribution should be given by the Boltzmann weights $P_{\rm st}(x) \propto e^{-V(x)/k_{\rm B}T}$. In order to confirm this, we study the corresponding Fokker–Planck equation, called *Smoluchowski equation* in this context. With $\xi(t) = x(t+\tau) - x(t) \approx \Gamma F(x)\tau + \int_t^{t+\tau} r(t')\,dt'$, we find $\langle\xi(t)\rangle \approx \Gamma F(x)\tau$ and $\langle\xi_i(t)\xi_j(t)\rangle \approx (\Gamma\tau)^2 F_i F_j + 2\Gamma\,k_{\rm B}T\,\delta_{ij}\int_t^{t+\tau}dt'\int_t^{t+\tau}dt''\delta(t-t') =$

$2\Gamma\, k_{\rm B}T\, \delta_{ij}\tau + O(\tau^2)$, while all higher moments are at least of order τ^2. The only non-vanishing Kramers–Moyal coefficients are therefore $\alpha_1(x) = \Gamma F(x)$ and $\alpha_{ij}(x) = 2\Gamma\, k_{\rm B}T\, \delta_{ij}$, and we obtain the Smoluchowski equation

$$\frac{\partial P_1(x,t)}{\partial t} = -\Gamma\, \frac{\partial}{\partial x} \cdot \left[F(x) P_1(x,t) - k_{\rm B}T\, \frac{\partial P_1(x,t)}{\partial x} \right] \tag{2.160}$$

(for a direct derivation, see Prob. 2.9). Indeed, stationarity requires the probability current $J_1(x,t) = \Gamma[F(x)\, P_1(x,t) - k_{\rm B}T\, \partial P_1(x,t)/\partial x]$ to vanish, which is satisfied by the canonical distribution

$$P_{\rm st}(x) = \frac{e^{-V(x)/k_{\rm B}T}}{\int e^{-V(x)/k_{\rm B}T}\, d^d x} \ . \tag{2.161}$$

For example, let us consider a harmonic potential $V(x) = \frac{f}{2}\, x^2$, $F(x) = -f\, x$. With the substitutions $x \leftrightarrow v$, $f \leftrightarrow m$, and $f\Gamma \leftrightarrow \zeta$, the associated Smoluchowski equation (2.160) becomes identical with the Fokker–Planck equation (2.147) for free Brownian motion. For the sharp initial condition $P_1(x,0) = \delta(x - x_0)$, naturally $P_1(x,t) = P_{1|1}(x,t|x_0,0)$, and with Eq. (2.141) we obtain from Eq. (2.153),

$$P_{1|1}(x,t|x_0,0) = \left[\frac{f}{2\pi\, k_{\rm B}T\, (1 - e^{-2f\Gamma t})} \right]^{d/2} \exp\left[- \frac{f(x - x_0\, e^{-f\Gamma t})^2}{2\, k_{\rm B}T (1 - e^{-2f\Gamma t})} \right] . \tag{2.162}$$

The general solution for an arbitrary normalized initial distribution $w_0(x)$ reads

$$P_1(x,t) = \int P_{1|1}(x,t|x',0)\, w_0(x')\, d^d x' \ , \tag{2.163}$$

which relaxes to thermal equilibrium

$$P_{\rm st}(x) = \left(\frac{f}{2\pi\, k_{\rm B}T} \right)^{d/2} e^{-fx^2/2k_{\rm B}T} \ , \tag{2.164}$$

independent of $w_0(x)$. Upon adding an external force term $\Gamma h(t)$ and with $\gamma = \Gamma f$, the corresponding overdamped Langevin equation (2.157) becomes

$$\frac{\partial x(t)}{\partial t} = -\gamma\, x(t) + \Gamma\, h(t) + r(t) \ . \tag{2.165}$$

For $h = 0$, this is essentially Eq. (2.130) again.

An alternative long-time solution for this stochastic differential equation proceeds via direct Fourier transform, which immediately yields the dynamic response function (see also Prob. 2.2)

$$\chi_{ij}(\omega) = \frac{\partial \langle x_i(\omega) \rangle}{\partial h_j(\omega)} = \frac{\Gamma}{-i\omega + \gamma}\, \delta_{ij} = \chi(\omega)\, \delta_{ij} \ . \tag{2.166}$$

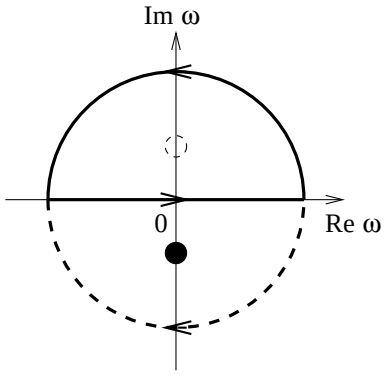

Fig. 2.11. Integration contours for the evaluation of the time-dependent response and correlation functions for an overdamped harmonic oscillator. The full and dashed circles denote the complex poles at $\omega = \mp i\gamma$, respectively.

We can now establish the causality property $\chi(t) = 0$ for $t < 0$. To this end we analyze the Fourier integral for $\chi(t)$ by means of the residue theorem. For $t < 0$, the exponential factor in the integrand forces us to close the integration contour in the complex upper half-plane Im $\omega > 0$ (full line in Fig. 2.11). But notice that $\chi(\omega)$ is analytic in the complex upper half-plane, and therefore the integral vanishes. For $t > 0$, on the other hand, the contour lies in the lower half-plane (dashed line in Fig. 2.11), and encloses the pole at $\omega = -i\gamma$ (full circle in Fig. 2.11). The Fourier integral thus yields

$$\chi(t) = \frac{i\Gamma}{2\pi} \int \frac{e^{-i\omega t}}{\omega + i\gamma}\, d\omega = \Gamma\, e^{-\gamma t}\, \Theta(t) \ . \tag{2.167}$$

With the aid of Eq. (2.158), we also readily compute the dynamic correlation function

$$\begin{aligned} \langle x_i(\omega) x_j(\omega') \rangle &= \frac{\langle r_i(\omega) r_j(\omega') \rangle}{(-i\omega + \gamma)(-i\omega' + \gamma)} = C(\omega)\, 2\pi\delta(\omega + \omega')\delta_{ij} \ , \\ C(\omega) &= \frac{2\Gamma\, k_{\mathrm{B}} T}{\omega^2 + \gamma^2} \ , \end{aligned} \tag{2.168}$$

since $\langle r_i(\omega) r_j(\omega') \rangle = 2\Gamma\, k_{\mathrm{B}} T\, 2\pi\delta(\omega + \omega')\delta_{ij}$. Upon comparing with Im $\chi(\omega)$, we see that the Einstein relation (2.158) guarantees the validity of the equilibrium fluctuation-dissipation theorem (2.35). Fourier backtransform gives

$$C(t) = \frac{\Gamma\, k_{\mathrm{B}} T}{\pi} \int \frac{e^{-i\omega t}}{\omega^2 + \gamma^2}\, d\omega = \frac{k_{\mathrm{B}} T}{f}\, e^{-\gamma |t|} \ , \tag{2.169}$$

in accord with Eqs. (2.36) and (2.167). Finally, we explicitly confirm the

classical equipartition theorem

$$\frac{f}{2}\,\langle x(t)^2\rangle = f\,\frac{d}{2}\,C(t=0) = \frac{d}{2}\,k_{\mathrm{B}}T\ . \tag{2.170}$$

Probs. 2.10 and 2.11 address related applications to electrical LRC circuits and a semi-classical description of single-mode lasers.

Quite generally in one dimension, the ansatz $P_1(x,t) = \rho(x,t)\,e^{-V(x)/2k_{\mathrm{B}}T}$ transforms the Smoluchowski equation (2.160) to a Schrödinger equation in imaginary time (with $\tau = -i\hbar 2\Gamma\,k_{\mathrm{B}}T\,t$):

$$\frac{\partial\rho(x,t)}{\partial t} = 2\Gamma\,k_{\mathrm{B}}T\left[\frac{1}{2}\,\frac{\partial^2}{\partial x^2} - V^0(x)\right]\rho(x,t)\ , \tag{2.171}$$

with the potential $V^0(x)$ and its 'supersymmetric' partner $V^1(x)$ defined through

$$V^{0/1}(x) = \frac{V'(x)^2}{8(k_{\mathrm{B}}T)^2} \mp \frac{V''(x)}{4k_{\mathrm{B}}T}\ . \tag{2.172}$$

Variable separation $\rho(x,t) = \sum_n c_n\phi_n^{0/1}(x)\,e^{-2\Gamma\,k_{\mathrm{B}}T\,\epsilon_n^{0/1}t}$ leads to the eigenvalue problems

$$\left[-\frac{1}{2}\,\frac{\partial^2}{\partial x^2} + V^{0/1}(x)\right]\phi_n^{0/1}(x) = \epsilon_n^{0/1}\phi_n^{0/1}(x)\ . \tag{2.173}$$

'Supersymmetric' quantum mechanics[5] now states that the spectrum belonging to the potential $V^1(x)$ coincides with all the *excited* states for $V^0(x)$, $\epsilon_n^1 = \epsilon_n^0$ for $n > 0$. The latter has the additional normalized ground state

$$\phi_0^0(x) = \frac{e^{-V(x)/2k_{\mathrm{B}}T}}{\left(\int e^{-V(x)/k_{\mathrm{B}}T}\,dx\right)^{1/2}}\ , \tag{2.174}$$

with $\epsilon_0^0 = 0$, as is readily confirmed by direct calculation. Hence all $\epsilon_n^0 > 0$ for $n > 0$, and with the coefficient

$$c_0 = \int \phi_0^0(x)\rho(x,t)\,dx = \frac{\int P_1(x,t)\,dx}{\left(\int e^{-V(x)/k_{\mathrm{B}}T}\,dx\right)^{1/2}} = \frac{1}{\left(\int e^{-V(x)/k_{\mathrm{B}}T}\,dx\right)^{1/2}}$$

we obtain

$$P_1(x,t) = \frac{e^{-V(x)/k_{\mathrm{B}}T}}{\int e^{-V(x)/k_{\mathrm{B}}T}\,dx} + e^{-V(x)/2k_{\mathrm{B}}T}\sum_{n>0} c_n\phi_n^0(x)\,e^{-2\Gamma\,k_{\mathrm{B}}T\,\epsilon_n^0 t}\ , \tag{2.175}$$

which approaches the Boltzmann factor (2.161) as $t \to \infty$.

At last we return to the general Langevin equation (2.156). Treating $x(t)$

[5] See, e.g., Schwabl (2007), Chap. 19.

and $v(t)$ as independent variables, this second-order differential equation is transformed to a first-order one for the $2d$-dimensional vector (x, v),

$$\begin{aligned} \frac{\partial x(t)}{\partial t} &= v(t) \ , \\ m\,\frac{\partial v(t)}{\partial t} &= -m\zeta\, v(t) + F(x) + f(t) \ . \end{aligned} \tag{2.176}$$

At time t, the stochastic process is then characterized by the joint probability distribution

$$P_1(x, v, t) = \Big\langle \delta\Big(x - x(t)\Big)\, \delta\Big(v - v(t)\Big) \Big\rangle \ . \tag{2.177}$$

With $\partial x(t)/\partial t = v(t)$,

$$\begin{aligned} \frac{\partial P_1(x,v,t)}{\partial t} &= -\frac{\partial}{\partial x} \cdot \Big\langle \delta\Big(x - x(t)\Big)\, \delta\Big(v - v(t)\Big) v(t) \Big\rangle \\ &\quad - \frac{\partial}{\partial v} \cdot \Big\langle \delta\Big(x - x(t)\Big)\, \delta\Big(v - v(t)\Big) \left[-\zeta v(t) + \frac{F(x)}{m} + \frac{f(t)}{m} \right] \Big\rangle \\ &= -v \cdot \frac{\partial P_1(x,v,t)}{\partial x} + \zeta\, \frac{\partial}{\partial v} \left[v \cdot P_1(x,v,t) \right] - \frac{F(x)}{m} \cdot \frac{\partial P_1(x,v,t)}{\partial v} \\ &\quad - \frac{1}{m}\, \frac{\partial}{\partial v} \cdot \Big\langle \delta\Big(x - x(t)\Big)\, \delta\Big(v - v(t)\Big) f(t) \Big\rangle \ , \end{aligned} \tag{2.178}$$

and the last term can be evaluated further as in Eqs. (2.149) and (2.150). The resulting general Fokker–Planck equation for Brownian motion in an external field $F(x)$ becomes

$$\begin{aligned} &\frac{\partial P_1(x,v,t)}{\partial t} + v \cdot \frac{\partial P_1(x,v,t)}{\partial x} + \frac{F(x)}{m} \cdot \frac{\partial P_1(x,v,t)}{\partial v} \\ &\qquad = \zeta\, \frac{\partial}{\partial v} \cdot \left[v\, P_1(x,v,t) + \frac{\lambda}{2\zeta m^2}\, \frac{\partial P_1(x,v,t)}{\partial v} \right] \ . \end{aligned} \tag{2.179}$$

The left-hand side of this partial differential equation represents the deterministic part; with no fluid of light particles present, it just represents Liouville's equation for the phase space density of classical non-interacting particles. The dissipative and stochastic terms on the right-hand side stem from the collisions with the fluid particles. Provided Einstein's relation (2.141) is fulfilled, the stationary solution to Eq. (2.179) reads

$$P_{\mathrm{st}}(x, v) = \frac{1}{Z(T)}\ \exp\!\left[-\frac{V(x)}{k_{\mathrm{B}}T}\ -\ \frac{m v^2}{2 k_{\mathrm{B}} T} \right] , \tag{2.180}$$

with the classical canonical partition function

$$Z(T) = \left(\frac{2\pi\, k_{\mathrm{B}} T}{m} \right)^{d/2} \int e^{-V(x)/k_{\mathrm{B}}T}\, d^d x \ . \tag{2.181}$$

2.4.4 Markovian character and equilibrium conditions

We end this introduction to stochastic differential equations with some general considerations. Langevin equations take the form

$$\frac{\partial x(t)}{\partial t} = F[x(t)] + r(t) \ , \tag{2.182}$$

where $F(x)$ is a random function, and x may be a (possibly large) vector. Indeed, if higher time derivatives occur, we may incorporate $y(t) = \dot{x}(t)$ etc. into an enlarged vector x, with non-trivial couplings between its entries, and thus generically arrive (2.182), compare Eqs. (2.176). The solution $\{x(t)\}$ to this equation may be viewed as a stochastic process. It is of Markovian character, if and only if (after incorporating the average $\langle r \rangle$ into F) $r(t)$ represents Gaussian white noise,

$$\langle r(t) \rangle = 0 \ , \quad \langle r_i(t) r_j(t') \rangle = \lambda_i \delta_{ij} \delta(t - t') \ . \tag{2.183}$$

Roughly, the deterministic part of Eq. (2.182) is a first-order differential equation, and $x(t + \tau)$ follows from $x(t)$ only. The delta-correlated white noise implies that the stochastic part induces no memory at all. For a more formal proof, we recall that the temporal derivatives are defined here as the limit $\tau \to 0$ of discrete time steps in forward discretization $\partial x(t)/\partial t = \lim_{\tau \to 0} [x(t + \tau) - x(t)]/\tau$.[6] For the second moment of these increments one finds

$$\frac{1}{\tau^2} \Big\langle [x_i(t + \tau) - x_i(t)][x_j(t' + \tau) - x_j(t')] \Big\rangle = F_i[x(t)] F_j[x(t')] + \langle r_i(t) r_j(t') \rangle \ , \tag{2.184}$$

which factorizes for $t \neq t'$ (only) if (2.183) holds. The statements in Prob. 2.4 then establish the Markovian character.

The noise trajectory $\{r(t)\}$ of course represents a stochastic process itself. If we take its correlations to be

$$\langle r(t) \rangle = 0 \ , \quad \langle r_i(t) r_j(t') \rangle = \frac{\lambda_i \gamma}{2} \, e^{-\gamma |t - t'|} \, \delta_{ij} \ , \tag{2.185}$$

then the solution for the associated Langevin equation (2.182) represents a non-Markovian *Ornstein–Uhlenbeck process*. The stochastic process $\{r(t)\}$, on the other hand, can be obtained as the solution of the Langevin equation

$$\frac{\partial r(t)}{\partial t} = -\gamma \, r(t) + \eta(t) \ , \tag{2.186}$$

with Gaussian white noise $\eta(t)$ precisely of the form (2.183). For, if we

[6] Ambiguities can arise only in situations where the stochastic forces r or their correlators are functionals of the random variables $x(t)$ themselves; in such a situation, a more microscopic approach is called for, see Chap. 9.

recall Eqs. (2.139) and (2.140), we see that the solution of Eq. (2.186) reads $r(t) = e^{-\gamma t} \int_0^t e^{\gamma t'} \, \eta(t') \, dt'$, leading to

$$\langle r_i(t) r_j(t') \rangle = \frac{\lambda_i \gamma}{2} \left[e^{-\gamma |t-t'|} - e^{-\gamma (t+t')} \right] \delta_{ij} \ ,$$

which reduces to (2.185) for $t, t' \gg 1/\gamma$. The two *coupled* Langevin equations (2.182) and (2.186) therefore do constitute a Markov process. However, upon eliminating $r(t)$ as an independent variable, this Markovian character is lost.

Given an (effective) Hamiltonian $H(x)$, we may separate the 'reversible' forces $F_{\rm rev}(x)$ from the dissipative terms that describe relaxation towards a minimum of H,

$$F_{\rm rel}(x) = -\Gamma \, \frac{\partial H(x)}{\partial x} \ , \tag{2.187}$$

where Γ denotes the corresponding Onsager coefficient. The Langevin equation (2.182) now reads

$$\frac{\partial x(t)}{\partial t} = F_{\rm rev}[x(t)] - \Gamma \, \frac{\delta H[x]}{\delta x(t)} + r(t) \ . \tag{2.188}$$

Furthermore, we impose the noise correlations $\langle r_i(t) r_j(t') \rangle = \phi(t-t') \, \delta_{ij}$. As before, the associated Kramers–Moyal coefficients are readily found:

$$\alpha_1(x) = F(x) = F_{\rm rev}(x) - \Gamma \, \frac{\partial H(x)}{\partial x} \ , \tag{2.189}$$

$$\alpha_{ij} = \frac{1}{\tau} \int_t^{t+\tau} dt' \int_t^{t+\tau} dt'' \, \phi(t-t') \, \delta_{ij} \to \phi(\omega = 0) \, \delta_{ij} \tag{2.190}$$

in the limit of time scale separation, $\tau \gg \tau_c$. This yields the Fokker–Planck equation in the usual form of a continuity equation (2.92), with the probability current

$$J_1(x) = \left[F_{\rm rev}(x) - \Gamma \, \frac{\partial H(x)}{\partial x} \right] P_1(x,t) - \frac{\lambda}{2} \, \frac{\partial P_1(x,t)}{\partial x} \ , \tag{2.191}$$

where $\lambda = \phi(\omega = 0)$. For $P_1(x,t)$ to approach the stationary, canonical distribution (2.86) as $t \to \infty$, we see that there are *two* sufficient conditions, namely first the *Einstein relation*

$$\lambda = \int \phi(t) \, dt = 2 \Gamma \, k_{\rm B} T \tag{2.192}$$

for the dissipative terms; and second, we need to demand that the reversible stationary probability current be *divergence-free*,

$$\frac{\partial}{\partial x} \cdot \left[F_{\rm rev}(x) \, e^{-H(x)/k_{\rm B}T} \right] = 0 \ . \tag{2.193}$$

The first equilibrium condition is actually often the less stringent one; for, as long as the noise strength λ and the Onsager coefficient Γ are proportional, Eq. (2.192) may serve as the definition of an *effective* temperature T'. Yet for a genuinely non-equilibrium stationary state, at least one of these two conditions is violated, and the different contributions in (2.191) must balance each other in a highly non-trivial manner.

Problems

2.1 *Linear response functions with temporal operator derivatives.*
For $\dot{A}(t) = dA(t)/dt$ and $t \geq 0$, derive the identity $\Phi_{\dot{A}B}(t) = -\chi_{AB}(t)$, provided that $A(t)$ and $B(t')$ are uncorrelated as $|t - t'| \to \infty$. As consequences, establish the important relations $\Phi_{\dot{A}B}(\omega) = -i\omega\,\Phi_{AB}(\omega) - \chi_{AB}(\omega = 0)$ and $\chi_{\dot{A}B}(\omega = 0) = -\frac{i}{\hbar}\,\langle [A, B]\rangle_0$.

2.2 *Dynamic response functions for a damped harmonic oscillator.*
A driven classical harmonic oscillator is described by the equation of motion

$$m\Big(\frac{d^2}{dt^2} + \gamma\,\frac{d}{dt} + \omega_0^2\Big)x(t) = h(t)\ .$$

Here, γ denotes the friction coefficient, ω_0 the eigenfrequency of the free, undamped oscillator, and $h(t)$ the external driving force. Determine the dynamic susceptibility $\chi(\omega) = \partial\langle x(\omega)\rangle/\partial h(\omega)$, its reactive and dissipative components, the relaxation function $\Phi(\omega)$, and the dynamic correlation function $C(\omega)$.

2.3 *Density response sum rules.*
(a) For N particles confined to a volume V, derive the *compressibility sum rule*

$$\lim_{q\to 0}\,\mathcal{P}\int\frac{d\omega}{\pi}\,\frac{\chi''_{nn}(q,\omega)}{\omega} = \frac{N^2}{V}\,\kappa_T\ .$$

(b) For N particles of mass m, demonstrate the *f-sum rule*

$$\int\frac{d\omega}{2\pi}\,\omega\,\chi''_{nn}(q,\omega) = \frac{Nq^2}{2m}\ .$$

Hint: Use the continuity equation with the particle current operator $j(x,t) = \frac{\hbar}{2mi}\sum_{i=1}^{N}\Big\{\nabla_i, \delta\Big(x - x_i(t)\Big)\Big\}$.

2.4 *Markovian character and factorization of moments.*
(a) For a Markov chain, show that $\langle [x(t+\tau)-x(t)][x(t'+\tau)-x(t')]\rangle = \langle x(t+\tau)-x(t)\rangle\langle x(t'+\tau)-x(t')\rangle$ for $t \neq t'$.
(b) Now assume the factorization of the second moments for all possible arguments for $t \neq t'$, and demonstrate that Eq. (2.60) holds for $n = 3, 4$. Thus establish the Markovian character for a *Gaussian* stochastic process with *uncorrelated* increments.

2.5 *Master and Fokker–Planck equations for Markov processes.*
By means of the Chapman–Kolmogorov equation (2.61), derive
(a) the master equation (2.73), and
(b) the Fokker–Planck equation for $P_{1|1}(x,t|x_0,t_0)$
for Markovian processes with time-independent transition rates.

2.6 *Particle number fluctuations in the population dynamics model.*
(a) Compute the mean-square particle number fluctuations for the population dynamics model of Sec. 2.3.2 for $\sigma \neq \kappa$:

$$(\Delta n)^2 = \langle n(t)^2\rangle - \langle n(t)\rangle^2 = n_0\,\frac{\kappa+\sigma}{\kappa-\sigma}\,e^{(\sigma-\kappa)t}\left(1-e^{(\sigma-\kappa)t}\right) \ .$$

(b) Confirm $(\Delta n)^2 = 2n_0\kappa t$ at the extinction threshold $\sigma = \kappa$.

2.7 *Spontaneous particle creation and death processes.*
(a) Write down the master equation for the competing processes $\emptyset \to A$ (rate τ) and $A \to \emptyset$ (rate κ), and derive the partial differential equation

$$\frac{\partial g(x,t)}{\partial t} = (1-x)\left[\kappa\,\frac{\partial g(x,t)}{\partial x} - \tau g(x,t)\right]$$

for the generating function $g(x,t)$.
(b) Find the stationary solution $g_\infty(x) = g(x, t\to\infty)$, and subsequently determine the full time-dependent function $g(x,t)$, if initially n_0 particles are present.
(c) Compute the survival probability $P_a(t)$ and the mean particle number $\langle n(t)\rangle$ at time t.

2.8 *Langevin equation energy balance.*
For the Langevin equation (2.130), show that stationarity of the kinetic energy along with the classical equipartition theorem imply the Einstein relation (2.141).

2.9 *Direct derivation of Smoluchowski's equation.*
Derive the Smoluchowski equation (2.160) starting from the identity $P_1(x,t) = \Big\langle \delta\Big(x - x(t)\Big)\Big\rangle$, using the Langevin equation (2.157).

2.10 *LRC circuit and Nyquist's theorem.*
An LRC circuit consists of a resistor (resistance R), capacitor (capacitance C), and inductive coil (inductivity L).
(a) Show that at fixed temperature T, with an external voltage $V_{\rm ext}(t)$, and taking *thermal voltage noise* $V_{\rm th}$ into account, the capacitor charge $Q(t)$ obeys the Langevin equation

$$L\,\frac{\partial^2 Q(t)}{\partial t^2} + R\,\frac{\partial Q}{\partial t} + \frac{Q(t)}{C} = V_{\rm ext}(t) + V_{\rm th}(t)\ .$$

Comparing with Prob. 2.2, determine the dynamic response function $\chi(\omega) = \partial\langle Q(\omega)\rangle/\partial V_{\rm ext}(\omega)$, and its Fourier transform $\chi(t)$.
(b) For vanishing battery potential $V_{\rm ext} = 0$, compute the voltage and current correlations, and confirm *Nyquist's theorem*

$$\frac{C}{2}\left\langle V_c(t)^2\right\rangle = \frac{k_{\rm B}T}{2} = \frac{L}{2}\left\langle I_c(t)^2\right\rangle\ .$$

2.11 *Semi-classical description of a single-mode laser.*
Semi-classically, a single-mode laser is described by a complex electric field $E(t) = |E(t)|\,e^{i\varphi(t)}$. Including statistical (non-thermal) field fluctuations $F(t)$, the relevant equation of motion reads

$$\frac{\partial E(t)}{\partial t} = -\kappa E(t) + \Big[\alpha - \beta\,|E(t)|^2\Big]\,E(t) + F(t)\ ,$$

with positive coefficients κ, α, and β. They govern, respectively, losses due to absorption, reflections, etc.; the intensity gain which is proportional to the level inversion; and the saturation at high intensities. We further assume $\langle F(t)\rangle = 0$ and $\langle F(t)F(t')^*\rangle = \Lambda\delta(t-t')$.
(a) As functions of the control parameters, determine the stable stationary solutions in the noiseless limit.
(b) Transform the associated Fokker–Planck equation to polar coordinates. Find the stationary probability distribution $P_{\rm st}(E)$.
(c) Below the lasing threshold, i.e., for $\kappa > \alpha$, linearize both the Langevin and Fokker–Planck equations, and determine the field fluctuations as well as $P_{\rm st}(E)$.
(d) Above threshold ($\kappa < \alpha$), similarly linearize about the non-trivial stationary solution. For the phase fluctuations, confirm that

$$\left\langle e^{i[\varphi(t)-\varphi(t')]}\right\rangle \approx e^{-\beta\Lambda|t-t'|/2(\alpha-\kappa)}\ .$$

Again compute and discuss the field fluctuations and $P_{\rm st}(E)$.

References

P.M. Chaikin and T.C. Lubensky, *Principles of condensed matter physics*, Cambridge University Press (Cambridge, 1995), Chaps. 7,8.
B. Cowan, *Topics in Statistical Mechanics*, Imperial College Press (London, 2005), Chap. 5.
M. Kardar, *Statistical physics of fields*, Cambridge University Press (Cambridge, 2007), Chap. 9.
R.K. Pathria, *Statistical mechanics*, Butterworth–Heinemann (Oxford, 2nd ed. 1996), Chap. 14.
L.E. Reichl, *A modern course in statistical physics*, Wiley–VCH (Weinheim, 3rd ed. 2009), Chap. 7.
F. Reif, *Fundamentals of statistical and thermal physics*, McGraw–Hill (Singapore, 18th ed. 1985), Chap. 15.
F. Schwabl, *Statistical mechanics*, Springer (Berlin, 2nd ed. 2006), Chap. 8.
F. Schwabl, *Quantum mechanics*, Springer (Berlin, 4th ed. 2007), Chap. 19.
F. Schwabl, *Advanced quantum mechanics*, Springer (Berlin, 4th ed. 2008), Chap. 4.
N.G. Van Kampen, *Stochastic processes in physics and chemistry*, North Holland (Amsterdam, 1981).
C.M. Van Vliet, *Equilibrium and non-equilibrium statistical mechanics*, World Scientific (New Jersey, 2nd ed. 2010), Chaps. 16,18,19.

Further reading

D. Forster, *Hydrodynamic fluctuations, broken symmetry, and correlation functions*, Addison-Wesley (Redwood City, 3rd ed. 1983).
H. Haken, *Synergetics*, Springer (Berlin, 3rd ed. 1983).
P.K. Krapivsky, S. Redner, and E. Ben-Naim, *A kinetic view of statistical physics*, Cambridge University Press (Cambridge, 2010).
R. Kubo, M. Toda, and N. Hashitsume, *Statistical physics II — Nonequilibrium statistical mechanics*, Springer (Berlin, 2nd ed. 1991).
S.W. Lovesey, *Condensed matter physics: Dynamic correlations*, 2nd ed., Benjamin–Cummings (Menlo Park, 1986).
L. Marro and R. Dickman, *Nonequilibrium phase transitions in lattice models*, Cambridge University Press (Cambridge, 1999).
D. Mukamel, *Phase transitions in nonequilibrium systems*, in: *Soft and fragile matter: Nonequilibrium dynamics, metastability and flow*, eds. M.E. Cates and M.R. Evans, Scottish Universities Summer School in Physics **53**, Institute of Physics Publ. (Bristol), 231–258 (2000).
M. Polettini, *Nonequilibrium thermodynamics as a gauge theory*, EPL **97**, 30003-1–6 (2012).
H. Risken, *The Fokker–Planck equation*, Springer (Heidelberg, 1984).
R. Zwanzig, *Nonequilibrium Statistical Mechanics*, Oxford University Press (Oxford, 2001).

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