IV.3.3 Caldeira–Leggett model

In this subsection, we introduce a simple microscopical model for the fluid in which the Brownian particle is immersed, which leads to a friction force proportional to the velocity.

IV.3.3 a Caldeira–Leggett Hamiltonian

Consider a "Brownian" particle of mass M, with position and momentum $x(t)$ and $p(t)$ respectively, interacting with a "bath" of N mutually independent harmonic oscillators with respective masses m_j, positions $x_j(t)$ and momenta $p_j(t)$. The coupling between the particle and each of the oscillators is assumed to be bilinear in their positions, with a coupling strength C_j. Additionally, we also allow for the Brownian particle to be in a position-dependent potential $V_0(x)$.

Under these assumptions, the Hamilton function of the system consisting of the Brownian particle and the oscillators reads

$$H = \frac{p^2}{2M} + V_0(x) + \sum_{j=1}^{N}\left(\frac{p_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2 x_j^2\right) - \sum_{j=1}^{N} C_j\, x_j\, x. \tag{IV.68a}$$

It is convenient to rewrite the potential V_0 as

$$V_0(x) = V(x) + \left(\sum_{j=1}^{N}\frac{C_j^2}{2m_j\omega_j^2}\right)x^2,$$

where the second term in the right member clearly vanishes when the Brownian particle does not couple to the oscillators. The Hamilton function (IV.68a) can then be recast as

$$\boxed{H = \frac{p^2}{2M} + V(x) + \sum_{j=1}^{N}\left[\frac{p_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2\left(x_j - \frac{C_j}{m_j\omega_j^2}\,x\right)^2\right].} \tag{IV.68b}$$

This Hamilton function—or its quantum-mechanical counterpart, which we shall meet again in § IV.4.1 c—is known as the *Caldeira*[bk]*–Leggett*[bl] *Hamiltonian* [50].

For a physical interpretation, it is interesting to rescale the characteristics of the bath oscillators, performing the change of variables

$$m_j \to m'_j = \frac{m_j}{\lambda_j^2}, \qquad x_j \to x'_j = \lambda_j x_j, \qquad p_j \to p'_j = \frac{p_j}{\lambda_j}, \qquad j = 1,\dots,N$$

with $\lambda_j \equiv \dfrac{m_j\omega_j^2}{C_j}$ dimensionless constants. The Hamiltonian (IV.68b) then becomes

$$H = \frac{p^2}{2M} + V(x) + \sum_{j=1}^{N}\left[\frac{p'^2_j}{2m'_j} + \frac{1}{2}m'_j\omega_j^2\left(x'_j - x\right)^2\right], \tag{IV.69}$$

i.e. the interaction term between the Brownian particle and each oscillator only depends on their relative distance. The Caldeira–Leggett Hamiltonian can thus be interpreted as that of a particle of mass m, moving in the potential V with (light) particles of masses m'_j attached to it by springs of respective spring constants $m'_j\omega_j^2$ [51].

[bk] A. Caldeira, born 1950 [bl] A. J. Leggett, born 1938

Coming back to the form (IV.68b) of the Hamilton function, the corresponding equations of motion, derived from the Hamilton equations (II.1), read

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = \frac{1}{M}\,p(t), \qquad \frac{\mathrm{d}p(t)}{\mathrm{d}t} = \sum_{j=1}^{N} C_j\left[x_j(t) - \frac{C_j}{m_j\omega_j^2}\,x(t)\right] - \frac{\mathrm{d}V\big(x(t)\big)}{\mathrm{d}x}, \tag{IV.70a}$$

$$\frac{\mathrm{d}x_j(t)}{\mathrm{d}t} = \frac{1}{M}\,p_j(t), \qquad \frac{\mathrm{d}p_j(t)}{\mathrm{d}t} = -m\omega_j^2 x_j(t) + C_j x(t), \tag{IV.70b}$$

which can naturally be recast as second-order differential equations for the positions $x(t)$, $x_j(t)$.

IV.3.3 b Free particle

Let us now assume that the Brownian particle is "free", in the sense that the potential V in the Hamiltonian (IV.68b) vanishes, $V(x) = 0$. In that case, the last term on the right-hand side of second equation of motion for the Brownian particle, Eq. (IV.70a), vanishes.

Integrating formally the equations of motion (IV.70b) for each oscillator between an initial time t_0 and time t, one obtains

$$x_j(t) = x_j(t_0)\cos\omega_j(t-t_0) + \frac{p_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0) + C_j\int_{t_0}^{t} x(t')\,\frac{\sin\omega_j(t-t')}{m_j\omega_j}\,\mathrm{d}t'.$$

Performing an integration by parts and rearranging the terms, one finds

$$x_j(t) - \frac{C_j}{m_j\omega_j^2}\,x(t) = \left[x_j(t_0) - \frac{C_j}{m_j\omega_j^2}\,x(t_0)\right]\cos\omega_j(t-t_0) + \frac{p_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0) - C_j\int_{t_0}^{t}\frac{p(t')}{M}\,\frac{\cos\omega_j(t-t')}{m_j\omega_j^2}\,\mathrm{d}t'.$$

This can then be inserted in the right member of the second equation of motion in Eq. (IV.70a). Combining with the first equation of motion giving $p(t)$ in function of $\mathrm{d}x(t)/\mathrm{d}t$, one obtains

$$\frac{\mathrm{d}^2x(t)}{\mathrm{d}t^2} + \int_{t_0}^{t}\left[\frac{1}{M}\sum_{j=1}^{N}\frac{C_j^2}{m_j\omega_j^2}\cos\omega_j(t-t')\right]\frac{\mathrm{d}x(t')}{\mathrm{d}t}\,\mathrm{d}t' = \frac{1}{M}\sum_{j=1}^{N} C_j\left[x_j(t_0)\cos\omega_j(t-t_0) + \frac{p_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0)\right] - \left[\frac{1}{M}\sum_{j=1}^{N}\frac{C_j^2}{m_j\omega_j^2}\cos\omega_j(t-t_0)\right]x(t_0). \tag{IV.71}$$

Introducing the quantities

$$\gamma(t) \equiv \frac{1}{M}\sum_{j=1}^{N}\frac{C_j^2}{m_j\omega_j^2}\cos\omega_j t \tag{IV.72a}$$

and

$$F_{\mathrm{L}}(t) \equiv \sum_{j=1}^{N} C_j\left[x_j(t_0)\cos\omega_j(t-t_0) + \frac{p_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0)\right], \tag{IV.72b}$$

which both only involve characteristics of the bath, Eq. (IV.71) becomes

$$M\frac{\mathrm{d}^2x(t)}{\mathrm{d}t^2} + M\int_{t_0}^{t}\gamma(t-t')\,\frac{\mathrm{d}x(t')}{\mathrm{d}t}\,\mathrm{d}t' = -M\gamma(t-t_0)x(t_0) + F_{\mathrm{L}}(t). \tag{IV.72c}$$

This evolution equation for the position—or equivalently the velocity, since $x(t_0)$ in the right-hand side is only a number—of the Brownian particle is exact, and follows from the Hamiltonian equations of motion without any approximation. It is obviously very reminiscent of the generalized Langevin equation (IV.61a), up to a few points, namely the lower bound of the integral, the term $-M\gamma(t-t_0)x(t_0)$, and the question whether $F_{\mathrm{L}}(t)$ as defined by relation (IV.72b) is a Langevin force.

The first two differences between Eq. (IV.61a) and Eq. (IV.72c), rewritten in terms of the velocity, are easily dealt with, by sending the arbitrary initial time t_0 to $-\infty$: anticipating on what we shall find below, the memory kernel $\gamma(t)$ vanishes at infinity for the usual choices for the distribution of the bath oscillator frequencies, which suppresses the contribution $-M\gamma(t-t_0)x(t_0)$.

In turn, the characteristics of the force $F_{\rm L}(t)$, Eq. (IV.72b), depend on the initial positions and momenta $\{x_j(t_0), p_j(t_0)\}$ of the bath oscillators at time t_0. Strictly speaking, if the latter are exactly known, then $F_{\rm L}(t)$ is a deterministic force, rather than a fluctuating one. When the number N of oscillators becomes large, the deterministic character of the force becomes elusive, since in practice one cannot know the variables $\{x_j(t_0), p_j(t_0)\}$ with infinite accuracy (see the discussion in Sec. II.1). In practice, it is then more fruitful to consider the phase-space density $\rho_N\big(t_0,\{q_j\},\{p_j\}\big)$, Eq. (II.3). Assuming that at t_0 the bath oscillators are in thermal equilibrium at temperature T, ρ_N at that instant is given by the canonical distribution

$$\rho_N\big(t_0,\{q_j\},\{p_j\}\big) = \frac{1}{Z_N(T)} \exp\left[-\frac{1}{k_BT}\sum_{j=1}^{N}\left(\frac{p_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2 x_j^2\right)\right].$$

Computing average values with this Gaussian distribution,[(69)] one finds that the force $F_{\rm L}(t)$ as given by Eq. (IV.72b) is a stationary Gaussian random process, with vanishing average value $\langle F_{\rm L}(t)\rangle = 0$ and the autocorrelation function

$$\langle F_{\rm L}(t)F_{\rm L}(t+\tau)\rangle = Mk_BT\gamma(\tau).$$

That is, $F_{\rm L}(t)$ has the properties of a Langevin force as discussed in § IV.1.1 b.

Remark: For $V(x) = 0$, the Hamilton function (IV.69) is invariant under global translations of all (Brownian and light) particles, since it only depends on relative distances. As a consequence, the corresponding total momentum $p + \sum_j p'_j$ is conserved.

IV.3.3 c Limiting case of a continuous bath

As long as the number N of bath oscillators is finite, the Caldeira–Leggett Hamiltonian (IV.68b) with $V(x) = 0$ [or with a harmonic potential $V(x) \propto x^2$] strictly speaking leads to a periodic dynamical evolution. As thus, it cannot provide an underlying microscopic model for Brownian motion.[(70)] The latter can however emerge if one considers the limit of an infinite number of bath degrees of freedom,[(71)] in particular if the oscillator frequencies span a continuous interval.

To provide an appropriate description for both finite- and infinite-N cases, it is convenient to introduce the *spectral density of the coupling to the bath*

$$J(\omega) \equiv \frac{\pi}{2}\sum_j \frac{C_j^2}{m_j\omega_j}\,\delta(\omega-\omega_j). \qquad \text{(IV.73)}$$

With its help, the memory kernel (IV.72a) can be recast as

$$\gamma(t) = \frac{2}{\pi}\int \frac{J(\omega)}{M\omega}\cos\omega t\,{\rm d}\omega. \qquad \text{(IV.74)}$$

[(69)] As noted in the remark at the end of § IV.1.1 b, this is indeed the meaning of expectation values in this chapter, since we are averaging over all microscopic configurations $\{x_j(t_0), p_j(t_0)\}$ compatible with a given macroscopic temperature.

[(70)] ... valid on any time scale. Physically, if $N \gg 1$, the Poincaré[(bm)] recurrence time of the system will in general be very large. On a time scale much smaller than this recurrence time, the periodicity of the problem can be ignored, and the dynamics is well described by the generalized Langevin model.

[(71)] The frequencies of the bath oscillators should not stand in simple relation to each other—as for instance if they were all multiples of a single frequency.

[(bm)] H. Poincaré, 1854–1912

If N is finite, then $J(\omega)$ is a discrete sum of δ-distributions. Let ε denote the typical spacing between two successive frequencies ω_j of the bath oscillators. For evolutions on time scales much smaller than $1/\varepsilon$, the discreteness of the set of frequencies may be ignored.(70) Consider the continuous function $J_c(\omega)$, such that on every interval $\mathcal{I}_\omega \equiv [\omega, \omega + \mathrm{d}\omega]$ of width $\mathrm{d}\omega \gg \varepsilon$, with $\mathrm{d}\omega$ small enough that $J_c(\omega)$ does not vary significantly over $\mathcal{I}_\omega$, one has

$$J_c(\omega)\,\mathrm{d}\omega = \sum_{\omega_j \in \mathcal{I}_\omega} \frac{\pi}{2} \frac{C_j^2}{m_j \omega_j}. \tag{IV.75}$$

One can then replace $J(\omega)$ by $J_c(\omega)$, for instance in Eq. (IV.74), which amounts to considering a continuous spectrum of bath frequencies.

The simplest possible choice for $J_c(\omega)$ consists in assuming that it is proportional to the frequency for positive values of ω. To be more realistic, one also introduces an upper cutoff frequency ω_c, above which J_c vanishes:

$$J_c(\omega) = \begin{cases} M\gamma\omega & \text{for } 0 \leq \omega \leq \omega_c, \\ 0 & \text{otherwise.} \end{cases} \tag{IV.76}$$

This choice leads at once with Eq. (IV.74) to $\gamma(t) = 2\gamma\delta_{\omega_c}(t)$, where

$$\delta_{\omega_c}(t) = \frac{1}{\pi} \frac{\sin \omega_c t}{t} \tag{IV.77}$$

is a function that tends to $\delta(t)$ as $\omega_c \to +\infty$ and only takes significant values on a range of typical width ω_c^{-1} around $t = 0$. ω_c^{-1} is thus the characteristic time scale of the memory kernel $\gamma(t)$.

Remarks:

∗ In the limit $\omega_c \to +\infty$, i.e. of an instantaneous memory kernel $\gamma(t) = 2\gamma\delta(t)$, the evolution equation (IV.72c) reduces to the Langevin equation [cf. (IV.1)] $M\ddot{x}(t) + M\gamma\dot{x}(t) = F_{\mathrm{L}}(t)$. As this is also the equation governing the electric charge in a RL circuit, the choice $J_c(\omega) \propto \omega$ at low frequencies is referred to as "ohmic bath". In turn, a harmonic bath characterized by $J_c(\omega) \propto \omega^\eta$ with $\eta < 1$ (resp. $\eta > 1$) is referred to as sub-ohmic (resp. super-ohmic).(72)

∗ Instead of a step function $\Theta(\omega_c - \omega)$ as in Eq. (IV.76), one may also use a smoother cutoff function to handle the ultraviolet modes in the bath, without affecting the physical results significantly.

IV.4 Quantum Brownian motion

In this section, we investigate a system consisting of a "heavy" particle interacting with a bath of many lighter particles at thermodynamic equilibrium—which provides a quantum-mechanical analogue to the problem of Brownian motion. We first introduce in § IV.4.1 a rather general Hamilton operator for such a system, and investigate in § IV.4.1 a some of the properties of the spectral functions relating the velocity and position of the heavy particle that follow from the symmetries of the Hamiltonian. We then exemplify how the general sum rules derived in § III.3.6 constrain the spectral function—and in particular show that Langevin dynamics based on Eq. (IV.1) cannot constitute the classical limit of such a model (§ IV.4.1 b). Eventually we focus on the case of the Caldeira–Leggett Hamiltonian already introduced in § IV.3.3, considered now at the quantum-mechanical level, and show that it describes a "quantum dissipative system" governed by a generalized Langevin equation (§ IV.4.1 c).

IV.4.1 Description of the system

Consider a heavy particle of mass M interacting with a "bath" of (many) identical light particles of mass m. For the sake of simplicity, we assume that the various particles only interact by pairs—be

(72) See Ref. [52] for a study in the non-ohmic case.

it for the heavy–light or light–light interactions—with potentials that depend only on the distance between the particles.

The Hamiltonian of the system thus reads

$$\hat{H}_0 = \frac{\hat{\vec{p}}^2}{2M} + \sum_j \frac{\hat{\vec{p}}_j^2}{2m} + \sum_{j\neq k} w\big(|\hat{\vec{r}}_j - \hat{\vec{r}}_k|\big) + \sum_j W\big(|\hat{\vec{r}} - \hat{\vec{r}}_j|\big), \tag{IV.78}$$

with $\hat{\vec{p}}$, $\hat{\vec{r}}$ the momentum and position of the heavy particle and $\hat{\vec{p}}_j$, $\hat{\vec{r}}_j$ those of the j-th particle of the bath, while w, W denote the interaction potentials for light–light and heavy–light pairs, respectively. In § IV.4.1 c, we shall consider the special case in which w and W are harmonic potentials.

Let $\hat{x}$, $\hat{y}$, $\hat{z}$ denote the components of $\hat{\vec{r}}$ in a given, fixed Cartesian coordinate system, and $\hat{p}_x$, $\hat{p}_y$, $\hat{p}_z$ the corresponding coordinates of momentum. Using definition (III.49), one can define the operators $\hat{\dot{x}}$, $\hat{\dot{y}}\ldots$, which using the Hamiltonian (IV.78) and the usual commutation relations are given by

$$\hat{\dot{x}} \equiv \frac{1}{\mathrm{i}\hbar}\big[\hat{x},\hat{H}_0\big] = \frac{\hat{p}_x}{M} = \hat{v}_x, \tag{IV.79}$$

and similarly in the other two space directions, where $\hat{v}_x$, $\hat{v}_y$, $\hat{v}_z$ are the components of the velocity of the heavy particle.

We investigate the effect of applying an external force, for instance along the x-direction, amounting to a perturbation of the Hamiltonian $\hat{W} = -f(t)\hat{x}$. The "output" consists of any component $\hat{v}_i$ of the heavy-particle velocity. Throughout this section, we shall omit the index I denoting the interaction-picture representation of observables, yet any time-dependent operator is to be understood as being in that representation.

IV.4.1 a Constraints from the symmetries of the system

The Hamilton operator (IV.78) is invariant under several transformations. From the invariance under spatial and temporal translations follow as usual the conservation of the total momentum and of energy. Yet in the spirit of § III.3.5 we also want to discuss the consequences of the invariance under several discrete symmetries for the time correlation functions of the system.

Consequence of spatial symmetries

We first want to show that correlation functions of the type $\xi_{v_y x}(t)$—describing the effect on $\hat{v}_y$ of a force acting along the x-direction—all identically vanish.

For that purpose, consider the reflection with respect to the xz-plane, which is described by a unitary operator $\hat{\mathscr{S}}_y$. This symmetry operation leaves the Hamiltonian $\hat{H}_0$, and thus the equilibrium density operator $\hat{\rho}_{\text{eq.}}$, invariant:

$$\hat{\mathscr{S}}_y\hat{H}_0\hat{\mathscr{S}}_y^\dagger = \hat{H}_0 \quad,\quad \hat{\mathscr{S}}_y\hat{\rho}_{\text{eq.}}\hat{\mathscr{S}}_y^\dagger = \hat{\rho}_{\text{eq.}}. \tag{IV.80a}$$

The reflection also leaves $\hat{x}$ invariant, yet it transforms $\hat{v}_y$ into $-\hat{v}_y$:

$$\hat{\mathscr{S}}_y\,\hat{x}\,\hat{\mathscr{S}}_y^\dagger = \hat{x} \quad,\quad \hat{\mathscr{S}}_y\,\hat{v}_y\,\hat{\mathscr{S}}_y^\dagger = -\hat{v}_y. \tag{IV.80b}$$

Eventually, since the operator $\hat{\mathscr{S}}_y$ is unitary, it transforms the eigenstates $\{\,|\phi_n\rangle\}$ of $\hat{H}_0$ into a set of states $\{\,|\hat{\mathscr{S}}_y\phi_n\rangle \equiv \hat{\mathscr{S}}_y\,|\phi_n\rangle\}$ which form an orthonormal basis.

We can now compute the equilibrium expectation value $\langle\hat{v}_y(t)\hat{x}\rangle_{\text{eq.}}$:

$$\begin{aligned}\mathrm{Tr}\big[\hat{\rho}_{\text{eq.}}\hat{v}_y(t)\hat{x}\big] &= \sum_n \big\langle\phi_n\big|\hat{\rho}_{\text{eq.}}\hat{v}_y(t)\hat{x}\big|\phi_n\big\rangle = \sum_n \big\langle\phi_n\big|\hat{\mathscr{S}}_y^\dagger\hat{\mathscr{S}}_y\hat{\rho}_{\text{eq.}}\hat{\mathscr{S}}_y^\dagger\hat{\mathscr{S}}_y\hat{v}_y(t)\hat{\mathscr{S}}_y^\dagger\hat{\mathscr{S}}_y\hat{x}\hat{\mathscr{S}}_y^\dagger\hat{\mathscr{S}}_y\big|\phi_n\big\rangle \\ &= \sum_n \big\langle\hat{\mathscr{S}}_y\phi_n\big|\big(\hat{\rho}_{\text{eq.}}\big)\big(-\hat{v}_y(t)\big)\big(\hat{x}\big)\big|\hat{\mathscr{S}}_y\phi_n\big\rangle = -\sum_n \big\langle\hat{\mathscr{S}}_y\phi_n\big|\hat{\rho}_{\text{eq.}}\hat{v}_y(t)\hat{x}\big|\hat{\mathscr{S}}_y\phi_n\big\rangle.\end{aligned}$$

Since the $\{\,|\hat{\mathscr{S}}_y\phi_n\rangle\}$ constitute an orthonormal basis, the last term is exactly the opposite of the trace of $\hat{\rho}_{\text{eq.}}\hat{v}_y(t)\hat{x}$, i.e. equals $-\langle\hat{v}_y(t)\hat{x}\rangle_{\text{eq.}}$. That is,

$$\langle \hat{v}_y(t)\hat{x}\rangle_{\text{eq.}} = -\langle \hat{v}_y(t)\hat{x}\rangle_{\text{eq.}} = 0,$$

from which one at once deduces

$$\xi_{v_y x}(t) = -\xi_{v_y x}(t) = 0. \tag{IV.81}$$

One shows in a similar way that only $\xi_{v_x x}$, $\xi_{v_y y}$ and $\xi_{v_z z}$ are non-zero.

Using the invariance of the Hamiltonian (IV.78) under arbitrary rotations, one can show that these three correlation functions are equal. This allows one to replace the problem of Brownian motion in three dimensions by three identical one-dimensional problems, as was done from the start in Chapter IV.

Invariance under time reversal

The Hamiltonian (IV.78) is clearly invariant under time reversal. Using Eq. (III.74), the reciprocity relation (III.77) then reads

$$\tilde{\xi}_{v_x x}(\omega) = -\tilde{\xi}_{x v_x}(\omega). \tag{IV.82}$$

Together with Eq. (III.54c), this shows that $\tilde{\xi}_{v_x x}(\omega)$ is purely imaginary and even in ω.

Considering now relation (III.79), one similarly finds

$$\tilde{\chi}_{v_x x}(\omega) = -\tilde{\chi}_{x v_x}(\omega).$$

Inserting this identity in Eq. (III.57), one finds

$$\tilde{\xi}_{v_x x}(\omega) = \frac{1}{2\mathrm{i}}\big[\tilde{\chi}_{v_x x}(\omega) - \tilde{\chi}_{x v_x}(\omega)^*\big] = \frac{1}{2\mathrm{i}}\big[\tilde{\chi}_{v_x x}(\omega) + \tilde{\chi}_{v_x x}(\omega)^*\big] = -\mathrm{i}\,\mathrm{Re}\,\tilde{\chi}_{v_x x}(\omega). \tag{IV.83}$$

Eventually, one can relate the spectral function $\tilde{\xi}_{v_x x}(\omega)$ for velocity–position correlations to the spectral function $\tilde{\xi}_{xx}(\omega)$ associated with position–position correlations, by Fourier transforming the identity

$$\xi_{v_x x}(t) = \frac{1}{2\hbar}\left\langle\left[\frac{\mathrm{d}\hat{x}(t)}{\mathrm{d}t},\hat{x}\right]\right\rangle_{\text{eq.}} = \frac{1}{2\hbar}\frac{\mathrm{d}}{\mathrm{d}t}\big\langle[\hat{x}(t),\hat{x}]\big\rangle_{\text{eq.}} = \frac{\mathrm{d}\xi_{xx}(t)}{\mathrm{d}t},$$

which gives

$$\tilde{\xi}_{v_x x}(\omega) = -\mathrm{i}\omega\tilde{\xi}_{xx}(\omega), \tag{IV.84}$$

which shows that $\tilde{\xi}_{xx}(\omega)$ is real and odd.

IV.4.1 b Fluctuation–dissipation theorem and sum rules

Thanks to relation (IV.79), the first fluctuation–dissipation theorem (III.65) with $\hat{A} = \hat{x}$ and $\hat{B} = \hat{v}_x$ reads

$$\tilde{\chi}_{v_x x}(\omega) = \frac{1}{k_B T}\int_0^\infty K_{v_x v_x}(t)\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t. \tag{IV.85}$$

This identity represents the quantum-mechanical generalization of relation (IV.40), which had been derived in a classical context, in which the Langevin equation is postulated phenomenologically, and in the equilibrium regime $t \gg \tau_{\mathrm{c}}$—which implicitly requires the separation of scales $\tau_{\mathrm{c}} \ll \tau_{\mathrm{r}}$.

Sum rules

To obtain a first sum rule, consider Eqs. (III.81)–(III.82) with $\hat{A} = \hat{x}$, $\hat{B} = \hat{v}_x$ and $k = l = 0$. This gives

$$\frac{1}{\hbar}\big\langle[\hat{v}_x,\hat{x}]\big\rangle_{\text{eq.}} = \frac{1}{\pi}\int_{-\infty}^{\infty}\tilde{\xi}_{v_x x}(\omega)\,\mathrm{d}\omega = -\mathrm{i}\beta K_{v_x v_x}(0). \tag{IV.86a}$$

Using $\hat{v}_x = \hat{p}_x/M$ and the usual commutator $\big[\hat{x},\hat{p}_x\big] = \mathrm{i}\hbar$, the left member of this equation is easily computed. The first identity then reads

$$\int_{-\infty}^{\infty}\tilde{\xi}_{v_x x}(\omega)\,\mathrm{d}\omega = -\frac{\mathrm{i}\pi}{M}, \tag{IV.86b}$$

which shows that that the integral of the spectral function is fixed. In turn, the identity between the first and third terms in the sum rule (IV.86a) gives

$$\frac{1}{2}MK_{v_xv_x}(0) = \frac{1}{2}k_BT, \tag{IV.86c}$$

which in the classical limit $K_{v_xv_x}(0) \underset{\hbar\to 0}{\to} \langle v_x^2\rangle$ is the equipartition theorem.

Taking now $k = 0$, $l = 1$, the sum rules (III.81)–(III.82) read

$$\frac{1}{\hbar^2}\Big\langle\Big[\hat{v}_x, \big[\hat{x}, \hat{H}_0\big]\Big]\Big\rangle_{\text{eq.}} = -\frac{1}{\pi}\int_{-\infty}^{\infty}\omega\,\tilde{\xi}_{v_xx}(\omega)\,\mathrm{d}\omega = \beta K_{\dot{v}_xv_x}(0), \tag{IV.87}$$

where in the rightmost term the canonical correlation function correlates the acceleration $\hat{\dot{v}}_x$ to the velocity $\hat{v}_x$.

The Hamiltonian (IV.78) yields the commutation relation $\big[\hat{x}, \hat{H}_0\big] = \mathrm{i}\hbar\hat{p}_x/M = \mathrm{i}\hbar\hat{v}_x$, so that the left member of Eq. (IV.87) equals zero. This means that the first moment of the spectral function vanishes—which was clear since $\tilde{\xi}_{v_xx}(\omega)$ is an even function. It also implies that the acceleration and the velocity at the same instant are not correlated, which is also a normal property for a stationary physical quantity and its time derivative.

Consider eventually the sum rule obtained when $k = l = 1$ and again $\hat{A} = \hat{x}$, $\hat{B} = \hat{v}_x$. In that case, Eqs. (III.81) and (III.82) yield

$$\frac{1}{\hbar^3}\Big\langle\Big[\big[\hat{v}_x, \hat{H}_0\big], \big[\hat{x}, \hat{H}_0\big]\Big]\Big\rangle_{\text{eq.}} = -\frac{1}{\pi}\int_{-\infty}^{\infty}\omega^2\,\tilde{\xi}_{v_xx}(\omega)\,\mathrm{d}\omega = \mathrm{i}\beta K_{\dot{v}_x\dot{v}_x}(0). \tag{IV.88a}$$

That is, the sum rule involves the second moment of the spectral function $\tilde{\xi}_{v_xx}(\omega)$ and the canonical autocorrelation function of the acceleration $\hat{\dot{v}}_x$ computed at equal times.

To compute the commutator on the left-hand side, one can first replace $\hat{v}_x$ by $\hat{p}_x/M$ and use as above $\big[\hat{x}, \hat{H}_0\big] = \mathrm{i}\hbar\hat{p}_x/M$, which gives

$$\frac{1}{\hbar^3}\Big\langle\Big[\big[\hat{v}_x, \hat{H}_0\big], \big[\hat{x}, \hat{H}_0\big]\Big]\Big\rangle_{\text{eq.}} = \frac{\mathrm{i}}{\hbar^2}\frac{1}{M^2}\Big\langle\Big[\big[\hat{p}_x, \hat{H}_0\big], \hat{P}_x\Big]\Big\rangle_{\text{eq.}}.$$

Using then

$$\big[\hat{p}_x, \hat{H}_0\big] = -\mathrm{i}\hbar\frac{\partial\hat{H}_0}{\partial\hat{x}} = -\mathrm{i}\hbar\frac{\partial\mathscr{V}(\hat{\vec{r}})}{\partial\hat{x}} \quad \text{with } \mathscr{V}(\hat{\vec{r}}) \equiv \sum_j W\big(|\hat{\vec{r}} - \hat{\vec{r}}_j|\big),$$

this becomes

$$\frac{1}{\hbar^3}\Big\langle\Big[\big[\hat{v}_x, \hat{H}_0\big], \big[\hat{x}, \hat{H}_0\big]\Big]\Big\rangle_{\text{eq.}} = \frac{1}{\hbar}\frac{1}{M^2}\bigg\langle\bigg[\frac{\partial\mathscr{V}(\hat{\vec{r}})}{\partial\hat{x}}, \hat{p}_x\bigg]\bigg\rangle_{\text{eq.}}.$$

Replacing again the commutator $\big[\hat{p}_x, \,\cdot\,\big]$ by $-\mathrm{i}\hbar\dfrac{\partial}{\partial\hat{x}}$, one eventually obtains

$$\frac{1}{\hbar^3}\Big\langle\Big[\big[\hat{v}_x, \hat{H}_0\big], \big[\hat{x}, \hat{H}_0\big]\Big]\Big\rangle_{\text{eq.}} = \frac{\mathrm{i}}{M^2}\bigg\langle\frac{\partial^2\mathscr{V}(\hat{\vec{r}})}{\partial\hat{x}^2}\bigg\rangle_{\text{eq.}}.$$

Invoking the invariance of the Hamiltonian (IV.78) under rotations, the second derivative with respect to x equals one third of the Laplacian, which all in all gives

$$\frac{1}{3M^2}\Big\langle\triangle\mathscr{V}(\hat{\vec{r}})\Big\rangle_{\text{eq.}} = \frac{\mathrm{i}}{\pi}\int_{-\infty}^{\infty}\omega^2\,\tilde{\xi}_{v_xx}(\omega)\,\mathrm{d}\omega = \beta K_{\dot{v}_x\dot{v}_x}(0). \tag{IV.88b}$$

This sum rule relates the potential in which the heavy particle is evolving, the second moment of the spectral function $\tilde{\xi}_{v_xx}(\omega)$ and the autocorrelation of the heavy-particle acceleration.

Comparison with the correlation functions of the Langevin model

The Langevin model investigated in Sec. IV.1 provides a classical, phenomenological description of the motion of a heavy particle, whose mass will hereafter be denoted as M, interacting with light particles. In particular, we studied in § IV.1.6 the time evolution of the heavy-particle velocity, averaged over many realizations of the motion, when the particle is submitted to an external force $F_{\text{ext.}}(t)$.

Now, the latter actually couples to the position x of the Brownian particle: the change in energy caused by the external force for a displacement Δx is simply the mechanical work $F_{\text{ext.}}\,\Delta x$.[73] Thus, the complex admittance characterizing the (linear!) response of the average velocity $\langle v_x\rangle$ to $F_{\text{ext.}}$ is, in the language of the present chapter, the generalized susceptibility $\chi_{v_x x}$. Equation (IV.39b) can therefore be rewritten as

$$\tilde{\chi}_{v_x x}(\omega) = \frac{1}{M}\frac{1}{\gamma - \mathrm{i}\omega}. \tag{IV.89}$$

According to relation (IV.83), this amounts to a spectral function

$$\tilde{\xi}_{v_x x}(\omega) = -\frac{\mathrm{i}}{M}\frac{\gamma}{\omega^2+\gamma^2}. \tag{IV.90}$$

One then easily checks that this phenomenological spectral function is purely imaginary and even [reciprocal relation (IV.82)] and that it fulfills the lowest-order sum rule (IV.86b). On the other hand, the second moment, as well as all higher moments, of $\tilde{\xi}_{v_x x}(\omega)$ diverges, so that the sum rule (IV.88b) cannot be satisfied.

This shows that the phenomenological Langevin equation (IV.1) does not describe the correct behavior at large frequencies, i.e. at short times. As already suggested in Sec. IV.3, this is due to the instantaneity of the friction force, which is simply proportional to the velocity at the same time.

IV.4.1 c Caldeira–Leggett model

In the previous paragraph, we have seen that the phenomenological Langevin model for the motion of a Brownian particle submitted to an external force yields correlation functions which do not fulfill the sum rules of linear-response theory. This means that the model can actually not be the macroscopic manifestation of an underlying microscopic dynamical model.[74]

From § IV.3.3, we already know that a classical heavy particle interacting with a bath of classical independent harmonic oscillators—which constitutes a special case of the model introduced in § IV.4.1—actually obeys a generalized Langevin equation when the bath degrees of freedom are integrated out. Here we want to consider this model again, now in the quantum-mechanical case.

Since the dynamics along different directions decouple, we restrict the study to a one-dimensional system, whose Hamilton operator is given by [cf. Eq. (IV.68b)]

$$\hat{H}_0 = \frac{\hat{p}^2}{2M} + \sum_{j=1}^{N}\left[\frac{\hat{p}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2\left(\hat{x}_j - \frac{C_j}{m_j\omega_j^2}\hat{x}\right)^2\right]. \tag{IV.91}$$

$\hat{x}$, $\hat{p}$, M are the position, momentum and mass of the heavy particle, while $\hat{x}_j$, $\hat{p}_j$ and m_j denote those of the harmonic oscillators, with resonant frequencies ω_j, with which the particle interacts.

Equations of motion

The Heisenberg equation (II.37) for the position and momentum of the heavy particle read

[73] This seemingly contrived formulation is used to avoid invoking some Hamilton function for the Langevin model, and its perturbation by the external force.

[74] More precisely, the Langevin equation cannot emerge as macroscopic limit valid on arbitrary time scales—or equivalently for all frequencies—of an underlying microscopic theory, although it might constitute an excellent approximation in a limited time / frequency range.

$$\frac{\mathrm{d}\hat{x}(t)}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar}\big[\hat{x}(t), \hat{H}_0\big] = \frac{1}{M}\hat{p}(t), \tag{IV.92a}$$

$$\frac{\mathrm{d}\hat{p}(t)}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar}\big[\hat{p}(t), \hat{H}_0\big] = \sum_{j=1}^{N} C_j \hat{x}_j(t) - \left(\sum_{j=1}^{N} \frac{C_j^2}{m_j\omega_j^2}\right)\hat{x}(t). \tag{IV.92b}$$

These equations are sometimes referred to as *Heisenberg–Langevin equations*.

The first term on the right hand side of the evolution equation for the momentum only depends on the bath degrees of freedom. Introducing the ladder operators $\hat{a}_j(t)$, $\hat{a}_j^\dagger(t)$ of the bath oscillators, it can be rewritten as

$$\hat{R}(t) \equiv \sum_{j=1}^{N} C_j \hat{x}_j(t) = \sum_{j=1}^{N} C_j \sqrt{\frac{\hbar}{2m_j\omega_j}}\Big[\hat{a}_j(t) + \hat{a}_j^\dagger(t)\Big]. \tag{IV.93}$$

The Heisenberg equation

$$\frac{\mathrm{d}\hat{a}_j(t)}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar}\big[\hat{a}_j(t), \hat{H}_0\big] = -\mathrm{i}\omega_j\hat{a}_j(t) + \mathrm{i}\frac{C_j}{\sqrt{2\hbar m_j\omega_j}}\hat{x}(t)$$

obeyed by the annihilation operator for the j-th oscillator admits the solution

$$\hat{a}_j(t) = \hat{a}_j(t_0)\,\mathrm{e}^{-\mathrm{i}\omega_j(t-t_0)} + \mathrm{i}\frac{C_j}{\sqrt{2\hbar m_j\omega_j}}\int_{t_0}^{t}\hat{x}(t')\,\mathrm{e}^{-\mathrm{i}\omega_j(t-t')}\,\mathrm{d}t',$$

with t_0 an arbitrary initial time. Inserting this expression and its adjoint in Eq. (IV.93), the evolution equation (IV.92b) becomes

$$\frac{\mathrm{d}\hat{p}(t)}{\mathrm{d}t} = \sum_{j=1}^{N}\frac{C_j^2}{2m_j\omega_j}\left[\mathrm{i}\int_{t_0}^{t}\hat{x}(t')\,\mathrm{e}^{-\mathrm{i}\omega_j(t-t')}\,\mathrm{d}t' + \mathrm{h.c.}\right] + \hat{F}_{\mathrm{L}}(t) - \left(\sum_{j=1}^{N}\frac{C_j^2}{m_j\omega_j^2}\right)\hat{x}(t), \tag{IV.94a}$$

where the operator $\hat{F}_{\mathrm{L}}(t)$ is defined as

$$\hat{F}_{\mathrm{L}}(t) \equiv \sum_{j=1}^{N} C_j\sqrt{\frac{\hbar}{2m_j\omega_j}}\Big[\hat{a}_j(t_0)\,\mathrm{e}^{-\mathrm{i}\omega_j(t-t_0)} + \hat{a}_j^\dagger(t_0)\,\mathrm{e}^{\mathrm{i}\omega_j(t-t_0)}\Big]. \tag{IV.94b}$$

This operator corresponds to a Langevin force, which only depends on freely evolving operators of the bath.[(75)] In turn, the first term on the right-hand side of Eq. (IV.94a) describes a retarded friction force exerted on the heavy particle by the bath, and due to the perturbation of the latter by the former at earlier times.

Limiting case of a continuous bath

Introducing as in § IV.3.3 c the *spectral density of the coupling to the bath*

$$J(\omega) \equiv \frac{\pi}{2}\sum_j \frac{C_j^2}{m_j\omega_j}\,\delta(\omega-\omega_j), \tag{IV.95}$$

and its continuous approximation $J_c(\omega)$ [cf. Eq. (IV.75)] the retarded force in Eq. (IV.94a) becomes

$$\sum_{j=1}^{N}\frac{C_j^2}{2m_j\omega_j}\left[\mathrm{i}\int_{t_0}^{t}\hat{x}(t')\,\mathrm{e}^{-\mathrm{i}\omega_j(t-t')}\,\mathrm{d}t' + \mathrm{h.c.}\right] = \frac{1}{\pi}\int J(\omega)\left[\mathrm{i}\int_{t_0}^{t}\hat{x}(t')\,\mathrm{e}^{-\mathrm{i}\omega(t-t')}\,\mathrm{d}t' + \mathrm{h.c.}\right]\mathrm{d}\omega$$
$$\simeq \frac{1}{\pi}\int J_c(\omega)\left[\mathrm{i}\int_{t_0}^{t}\hat{x}(t')\,\mathrm{e}^{-\mathrm{i}\omega(t-t')}\,\mathrm{d}t' + \mathrm{h.c.}\right]\mathrm{d}\omega, \tag{IV.96}$$

while the third term in that same equation can be rewritten as

(75) One easily checks in a basis of energy eigenstates $\langle\hat{a}_j(t_0)\rangle_{\mathrm{eq.}} = \langle\hat{a}_j^\dagger(t_0)\rangle_{\mathrm{eq.}} = 0$ for all bath oscillators, which results in $\langle\hat{F}_{\mathrm{L}}(t)\rangle_{\mathrm{eq.}} = 0$.

$$-\left(\sum_{j=1}^{N}\frac{C_j^2}{m_j\omega_j^2}\right)\hat{x}(t) = -\left(\frac{2}{\pi}\int\frac{J(\omega)}{\omega}\,\mathrm{d}\omega\right)\hat{x}(t) \simeq -\left(\frac{2}{\pi}\int\frac{J_c(\omega)}{\omega}\,\mathrm{d}\omega\right)\hat{x}(t). \tag{IV.97}$$

With a trivial change of integration variable from t' to $\tau = t-t'$ and some rewriting, the retarded force (IV.96) becomes after exchanging the order of integrations

$$\frac{1}{\pi}\int\frac{J_c(\omega)}{\omega}\left[\mathrm{i}\omega\int_0^{t-t_0}\hat{x}(t-\tau)\,\mathrm{e}^{-\mathrm{i}\omega\tau}\,\mathrm{d}t' + \text{h.c.}\right]\mathrm{d}\omega = -\frac{1}{\pi}\int_0^{t-t_0}\hat{x}(t-\tau)\,\frac{\mathrm{d}}{\mathrm{d}\tau}\left[\int\frac{J_c(\omega)}{\omega}\left(\mathrm{e}^{-\mathrm{i}\omega\tau}+\mathrm{e}^{\mathrm{i}\omega\tau}\right)\mathrm{d}\omega\right]\mathrm{d}\tau.$$

Introducing the "memory kernel" [cf. Eq. (IV.74)]

$$\gamma(\tau) \equiv \frac{2}{\pi}\int\frac{J_c(\omega)}{M\omega}\cos\omega\tau\,\mathrm{d}\omega \tag{IV.98}$$

and performing an integration by parts, in which the equation of motion (IV.92a) allows us to replace the time derivative of $\hat{x}(t)$ by $\hat{p}(t)/M$, the friction force becomes

$$-M\int_0^{t-t_0}\hat{x}(t-\tau)\,\gamma'(\tau)\,\mathrm{d}\tau = M\Big[\gamma(0)\hat{x}(t) - \gamma(t-t_0)\hat{x}(t_0)\Big] - \int_0^{t-t_0}\hat{p}(t-\tau)\,\gamma(\tau)\,\mathrm{d}\tau.$$

In many simple cases, corresponding to oscillator baths with a "short memory", the kernel $\gamma(\tau)$ only takes significant values in a limit range of size ω_c^{-1} around $\tau = 0$. As soon as $|t-t_0| \gg \omega_c^{-1}$, the term $\gamma(t-t_0)$ in the above equation then becomes negligible, while the upper limit of the integral can be sent to $+\infty$ without affecting the result significantly. Deducing $\gamma(0)$ from Eq. (IV.98), the friction force (IV.96) reads

$$\frac{1}{\pi}\int J_c(\omega)\left[\mathrm{i}\int_{t_0}^{t}\hat{x}(t')\,\mathrm{e}^{-\mathrm{i}\omega(t-t')}\,\mathrm{d}t' + \text{h.c.}\right]\mathrm{d}\omega = \left(\frac{2}{\pi}\int\frac{J_c(\omega)}{\omega}\,\mathrm{d}\omega\right)\hat{x}(t) - \int_0^{\infty}\hat{p}(t-\tau)\,\gamma(\tau)\,\mathrm{d}\tau.$$

The first term on the right hand side is exactly the negative of Eq. (IV.97): putting everything together, the evolution equation (IV.94a) takes the simple form of a generalized Langevin equation

$$\frac{\mathrm{d}\hat{p}(t)}{\mathrm{d}t} = -\int_0^{\infty}\hat{p}(t-\tau)\,\gamma(\tau)\,\mathrm{d}\tau + \hat{F}_{\mathrm{L}}(t). \tag{IV.99}$$

Dividing this equation by M, one obtains a similar evolution equation for the velocity operator $\hat{v}(t)$.

Generalized susceptibility

Let us add to the Hamiltonian (IV.91) a perturbation $\hat{W} = -F_{\text{ext.}}(t)\hat{x}(t)$ coupling to the position of the Brownian particle. One easily checks that this perturbation amounts to adding an extra term $F_{\text{ext.}}(t)\hat{\mathbb{1}}$ on the right-hand side of Eq. (IV.99). Dividing the resulting equation by M, taking the average, and Fourier transforming, one obtains the generalized susceptibility [cf. Eq. (IV.62)]

$$\tilde{\chi}_{vx}(\omega) = \frac{1}{M}\frac{1}{\tilde{\gamma}(\omega) - \mathrm{i}\omega}, \tag{IV.100a}$$

where $\tilde{\gamma}(\omega)$ is given by

$$\tilde{\gamma}(\omega) = \int\gamma(t)\,\Theta(t)\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t. \tag{IV.100b}$$

The Caldeira–Leggett Hamiltonian (IV.91) is invariant under time reversal. As already seen in § (IV.4.1 a), this leads to the proportionality between the spectral function $\tilde{\xi}_{vx}(\omega)$ and the real part of the generalized susceptibility $\tilde{\chi}_{vx}(\omega)$:

$$\tilde{\xi}_{vx}(\omega) = -\frac{\mathrm{i}}{M}\frac{\operatorname{Re}\tilde{\gamma}(\omega)}{|\tilde{\gamma}(\omega) - \mathrm{i}\omega|^2}.$$

If $\tilde{\gamma}(\omega)$ decreases quickly enough as $|\omega|$ goes to ∞—which depends on the specific behavior of $J_c(\omega)$ at infinity, see Eq. (IV.98)—, the spectral function $\tilde{\xi}_{vx}(\omega)$ can have moments to all orders, which can then obey the sum rules (III.81).