2

Relaxation, dissipation, noise and fluctuations

2.1 A simple model of Brownian motion

In this chapter we shall continue the study of relaxation, dissipation, noise and fluctuations by analyzing how they appear in simple models extracted from classical physics. We shall also introduce some specific concepts, such as the fluctuation–dissipation relation, which will be central to the development of our subject matter.

Possibly the simplest manifestation of the relaxation process is the damping of a pendulum swinging in open air. The simplest model of a pendulum is the harmonic oscillator

$$\ddot{x} + \Omega^2 x = 0 \tag{2.1}$$

At this level of description, it belongs to the realm of mechanics rather than thermodynamics [LanLif69]; it obeys the conservation of phase space volume theorem, it generates no entropy, and it does not relax. To see relaxation, we must introduce damping. Let us proceed phenomenologically by adding a "damping constant" γ to our oscillator equation (2.1), which becomes

$$\ddot{x} + 2\gamma\dot{x} + \Omega^2 x = 0 \tag{2.2}$$

Later we will probe into the microscopic origin of dissipation.

Introduce an angle φ such that $\gamma = \Omega \sin\varphi$ and write $\Omega_1 = \Omega\cos\varphi$. The solution to equation (2.2) is

$$x(t) = e^{-\gamma t}\left\{x(0)\frac{\cos[\Omega_1 t - \varphi]}{\cos\varphi} + \frac{p(0)}{M\Omega_1}\sin\Omega_1 t\right\} \tag{2.3}$$

where M is the mass of the oscillator. Although this system does relax, it is a little boring: the only possible equilibrium is at the bottom of the potential. But we know that a classical pendulum at finite temperature has nonzero average kinetic and potential energies, obeying the energy equipartition theorem. So something is missing. Let us call $\xi(t)$ the missing term, so that the system (2.2) becomes

$$\ddot{x} + 2\gamma\dot{x} + \Omega^2 x = \frac{\xi(t)}{M} \tag{2.4}$$

A solution is in the form $x = x_h + x_p$, where x_h is the homogeneous solution [given by equation (2.3)], and x_p is the particular solution

$$x_p(t) = \int_0^t dt'\, e^{-\gamma(t-t')}\frac{\sin\Omega_1(t-t')}{M\Omega_1}\xi(t') \tag{2.5}$$

Let us consider the source $\xi(t)$ as some kind of "noise" or stochastic forcing term, and assume that the expectation value at any time is zero $\langle \xi(t) \rangle = 0$, where $\langle\,\rangle$ stands for the average over realizations of the noise. Then $\langle x_p \rangle \equiv 0$, so that $\langle x \rangle \to 0$ as $t \to \infty$. As for $\left\langle x^2 \right\rangle$, we know that x_h will eventually die away, so for long times $\left\langle x^2(t) \right\rangle \sim \left\langle x_p^2(t) \right\rangle$, given by

$$\left\langle x_p^2(t) \right\rangle = \frac{1}{M^2\Omega_1^2} \int_0^t dt' dt''\, e^{-\gamma\left(2t-t'-t''\right)} \sin\Omega_1\left(t-t'\right) \sin\Omega_1\left(t-t''\right) \left\langle \xi\left(t'\right) \xi\left(t''\right) \right\rangle \tag{2.6}$$

To proceed we must say something about the noise correlator. If in our intuitive picture $\xi(t)$ represents the stochastic bombardment of the ball of the pendulum by its surrounding air molecules, then the simplest property is that the noise is stationary and statistically independent at macroscopically distinguishable times, hence $\langle \xi(t)\, \xi(t') \rangle = \sigma^2 \delta(t-t')$. Discarding exponentially decaying and other small terms, we obtain $\left\langle x^2(t) \right\rangle \sim \sigma^2/4M^2\Omega^2\gamma$. Comparing with the equipartition theorem $\left\langle x^2(t) \right\rangle = k_{\mathrm{B}}T/M\Omega^2$, where k_{B} is Boltzmann's constant, this suggests that the system is equilibrating at a temperature given by the Einstein relation [Ein05]

$$\sigma^2 = 4\gamma M k_{\mathrm{B}} T \tag{2.7}$$

We have succeeded (our model successfully describes relaxation) where we ought to have failed (we violated the time reversibility of the original model equation (2.1)). Let us take our model apart, and try to understand the secret of its working.

Observe that the system–environment interaction goes both ways: while the γ term steadily dumps system energy into the environment, whereby the information on initial conditions is lost, the noise term works in the opposite direction, feeding the right amount of fluctuations into the system and compensating its tendency to drop to the bottom of the potential. Neither alone would do the job, as clearly shown by equation (2.7), which, when seen in this light, goes under the name of a *fluctuation–dissipation theorem* [Nyq28, CalWel51].

In this view of the fluctuation–dissipation theorem, *if* we wish the system to relax at a certain temperature T, we'd better throw in white noise with the proper amplitude. But it could be that Nature does not care about relaxation, and therefore that it does not need a fluctuation–dissipation theorem. Well, as we know from everyday experience, it does, and there is a deeper reason for equation (2.7). In the final analysis, the Einstein relation is an expression of the unitarity of the dynamics of the system–environment complex. To understand how this comes about, we shall backtrack a little, and offer a simple mechanical model of how the environment works.

2.1.1 The linear oscillator model

The simplest possible mechanical model of the environment is to consider it as a large set of linear harmonic oscillators with displacement q_α, proper frequency ω_α

and mass m_α coupled to the system through a time-dependent coupling constant $c_\alpha(t)$ (see below) [Rub60, Rub61, FoKaMa65]. This is a very poor model of an environment; in a certain sense, it is no environment at all, as we may and will easily integrate the full dynamics, so there is little to be gained in regarding the q_α as different or "irrelevant," as the word "environment" may imply. In the real world, environments are huge nonlinear systems, and the information dumped in them is lost for all practical purposes as far as the observer is concerned. However, this modest ansatz for an environment will be adequate for our purpose here, which is why the above model actually works.

The full dynamics is given by

$$\begin{aligned}\ddot{x}(t)+\Omega^2 x(t)+\sum_\alpha \frac{c_\alpha(t)}{M} q_\alpha(t)&=0\\ \ddot{q}_\alpha(t)+\omega_\alpha^2 q_\alpha(t)+\frac{c_\alpha(t)}{m_\alpha}x(t)&=0\end{aligned} \tag{2.8}$$

The second set of equations is easily solved as $q_\alpha(t)=q_{\alpha p}(t)+q_{\alpha h}(t)$, where

$$\begin{aligned}q_{\alpha h}(t)&=\left[q_\alpha(0)+\frac{c_\alpha(0)}{m_\alpha\omega_\alpha^2}x(0)\right]\cos\omega_\alpha t+\frac{p_\alpha(0)}{m_\alpha\omega_\alpha}\sin\omega_\alpha t\\ q_{\alpha p}(t)&=\frac{-1}{m_\alpha\omega_\alpha}\int_0^t dt'\ \sin\omega_\alpha(t-t')\,c_\alpha(t')\,x(t')-\frac{c_\alpha(0)}{m_\alpha\omega_\alpha^2}x(0)\cos\omega_\alpha t\\ &=-\frac{c_\alpha(t)}{m_\alpha\omega_\alpha^2}x(t)+\frac{1}{m_\alpha\omega_\alpha^2}\int_0^t dt'\ \cos\omega_\alpha(t-t')\,\frac{d}{dt'}(c_\alpha x)\end{aligned} \tag{2.9}$$

We have kept this level of detail just to show that the evolution of the environment is not indifferent to the way the interaction is switched on. The simplest assumption is that the interaction is introduced adiabatically, but quickly settles to a constant value. In this scheme, we have $c_\alpha(0)=0$ but $\dot{c}_\alpha=0$ at any macroscopically positive time. Introducing this into the equation for the system, we obtain

$$\ddot{x}(t)+\int_0^t dt'\ \gamma(t-t')\,\dot{x}(t')+\Omega_r^2 x(t)=\frac{\xi(t)}{M} \tag{2.10}$$

where

$$\Omega_r^2=\Omega^2-\frac{1}{M}\sum_\alpha\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2} \tag{2.11}$$

$$\gamma(t-t')=\frac{1}{M}\sum_\alpha\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\cos\omega_\alpha(t-t') \tag{2.12}$$

$$\xi(t)=-\sum_\alpha c_\alpha q_{\alpha h}(t) \tag{2.13}$$

There are three differences between equations (2.10) and (2.4). First, the frequency of the system has been renormalized. The second difference is that γ now has a finite memory, reducing to the simple ohmic case $\gamma(t-t')=4\gamma\delta(t-t')$

only for a rather special (and unphysical) choice of the bath; this is unimportant for our present purpose. The real difference is that $\xi(t)$ is *not* a stochastic variable: it is a complex function of the bath's initial conditions. For this reason, equation (2.10) does *not* describe relaxation. It is simply the unitary dynamics of the system–bath complex, written in a different set of variables. So, what is missing?

Could it be that we forgot to record the actual initial conditions for the environment? If so, we may consider that these initial conditions are taken at random. To make it even simpler, we may assume that the initial conditions are taken independently for each oscillator, and that they sample each classical orbit homogeneously. Under these conditions, we have, from the classical virial theorem

$$\frac{1}{m_\alpha}\left\langle p_\alpha(0)\, p_{\alpha'}(0)\right\rangle = m_\alpha\omega_\alpha^2\left\langle q_\alpha(0)\, q_{\alpha'}(0)\right\rangle = \delta_{\alpha\alpha'}\left\langle \varepsilon_\alpha\right\rangle \tag{2.14}$$

$$\left\langle p_\alpha(0)\, q_{\alpha'}(0)\right\rangle = 0 \tag{2.15}$$

where $\langle\varepsilon_\alpha\rangle$ is the expectation value of the energy of the αth oscillator at $t = 0$. Now $\xi(t)$ is a bona fide stochastic variable, and

$$\left\langle \xi(t)\, \xi(t')\right\rangle = \sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\left\langle\varepsilon_\alpha\right\rangle \cos\omega_\alpha(t-t') \tag{2.16}$$

If the bath itself is at equilibrium, then $\langle\varepsilon_\alpha\rangle = k_{\mathrm{B}}T$, and $\langle\xi(t)\,\xi(t')\rangle = Mk_{\mathrm{B}}T\gamma(t-t')$. This is Einstein's relation for the non-ohmic case, reducing to the case above in the ohmic limit.

Somewhere between equations (2.13) and (2.16) the environment oscillators lose their role as dynamical variables. The "ordered" part of the system–environment energy transfer is replaced by the γ term in equation (2.10), which refers to the system alone (we say that the bath variables have been *slaved to the system*); the "disordered" part is replaced by a generic stochastic force, whose effect is to compensate the dissipation and thus to make a nontrivial steady equilibrium possible. Time-reversal invariance becomes devoid of operational meaning, because the choice of a random initial condition for the bath forfeits one's ability to reverse the initial velocities of each oscillator in the bath. This introduces an arrow of time in the macrodynamics.

Of course, the actual time development of $\xi(t)$ as given in equation (2.13) looks a lot like a realization of the stochastic process defined by equation (2.16) for any finite period. But as time goes by, correlations build up between the system and its environment which are not contained in the stochastic model. Because these correlations are neglected, the stochastic model describes a nonunitary evolution; therein lies the true reason for Boltzmann's H-theorem – if all correlations were kept, unitarity would be restored.

This basic framework for irreversibility will be the backdrop for our future discussions. Of course, the Brownian motion paradigm which we discussed here is an example of an *autocratic* system: the ball is the king, the relevant party, the center of attention, and the molecules in its environment are subservient, slaved and "irrelevant." Irreversibility also obtains in *democratic* systems, such as a Boltzmann gas: all molecules are born equal and treated equally. However, limitation of observational precision introduces coarse graining of a different sort. In particular, we shall see below how irreversibility in the Boltzmann gas is actually a consequence of the *slaving* of irrelevant, many-particle correlations to the one-particle distribution function, which is of special interest as the coarsest yet most accessible level of description.

2.1.2 Fluctuation–dissipation theorem

Let us discuss the fluctuation–dissipation theorem (FDT) in a still simple but more general framework. This formulation of the FDT will be relevant when we come to discuss fluctuations in the Boltzmann equation later on. This presentation follows closely that given by Landau and Lifshitz [LaLiPi80a].

The simplest setting for the FDT is a homogeneous system described by variables X^i. Equilibria are located at the maxima of a thermodynamic potential $S\left(X^i\right)$. For an isolated system, S is the entropy, for an isothermal system, $S = -F/k_{\rm B}T$, where F is the free energy, etc.

The thermodynamic forces are the components of the gradient of S, $L_i = -S_{,i}$ (a comma denotes a derivative). We chose coordinates so that thermodynamic equilibrium lies at $X^i = 0$. Then L_i also vanish at the origin, and for small deviations, we get a linear relationship $L_i = C_{ij}X^j$, where the matrix C is nonnegative.

For example, we could consider an isolated system made of a system proper and an environment. Let us choose as coordinates the energy, volume and particle number of the system $X^i = (E, V, N)$. The function S is the total entropy, and from the first law

$$dS = \left(\frac{1}{T_{\rm s}} - \frac{1}{T_{\rm e}}\right) dE + \left(\frac{p_{\rm s}}{T_{\rm s}} - \frac{p_{\rm e}}{T_{\rm e}}\right) dV - \left(\frac{\mu_{\rm s}}{T_{\rm s}} - \frac{\mu_{\rm e}}{T_{\rm e}}\right) dN \qquad (2.17)$$

where T, p and μ stand for temperature, pressure and chemical potential, and the subscripts "s" and "e" denote system and environment, respectively. The coefficients in this differential form are (minus) the forces, and we see that they indeed vanish at equilibrium. The matrix elements of C are the specific heat and compressibility functions, etc. (for example, $C_{EE} = 1/T^2C_V$), and the condition of C being nonnegative engenders a set of thermodynamic inequalities such as positivity of the specific heat.

We wish to motivate a dynamics for this system, under the basic requirement that it should describe regression to equilibrium. This suggests writing $\dot{X}^i = -\Gamma^{ij}L_j$, where Γ is nonnegative; then $\dot{S} = \Gamma^{ij}S_{,i}S_{,j} \geq 0$, and we obtain an H-theorem of sorts. But this dynamics is too efficient, because we know that in true equilibrium the system is not just sitting at $X = 0$, but fluctuating around it. Following Einstein, we identify the probability of a fluctuation carrying the system from 0 to X as $\exp S[X]$, whereby (in equilibrium) $\left\langle X^i L_j \right\rangle = \delta^i_j$. To obtain these fluctuations, we must modify our ansatz to

$$\dot{X}^i = -\Gamma^{ij} L_j + \Xi^i. \tag{2.18}$$

The first term describes the mean regression of the system towards a local entropy maximum, Γ^{ij} being the dissipative coefficient or function, and the second term describes the random microscopic fluctuations induced by its interaction with an environment. To simplify, let us assume that Ξ^i is a Gaussian white noise, namely $\left\langle \Xi^i(t)\, \Xi^j(t') \right\rangle = \sigma^{ij}\delta(t-t')$, where the matrix σ is, of course, symmetric and nonnegative. The FDT will allow us to relate the matrices σ and Γ.

In equilibrium, correlation functions are stationary. In particular

$$\frac{d}{dt}\left\langle X^i(t)\, X^j(t)\right\rangle = \left\langle \dot{X}^i(t)\, X^j(t) + X^i(t)\, \dot{X}^j(t)\right\rangle = 0 \tag{2.19}$$

Therefore

$$\left\langle \Xi^i(t)\, X^j(t) + X^i(t)\, \Xi^j(t)\right\rangle = \Gamma^{ij} + \Gamma^{ji} \tag{2.20}$$

If the noise is Gaussian, we have the Novikov identity [Nov65]

$$\left\langle X^i(t)\, \Xi^j(t')\right\rangle = \int dt''\, \frac{\delta X^i(t)}{\delta \Xi^k(t'')} \left\langle \Xi^k(t'')\, \Xi^j(t')\right\rangle \tag{2.21}$$

which for our chosen autocorrelation becomes

$$\left\langle X^i(t)\, \Xi^j(t')\right\rangle = \sigma^{kj} \frac{\delta X^i(t)}{\delta \Xi^k(t')} \tag{2.22}$$

Since the dynamics is linear, we may write

$$X^i(t) = X^i_h(t) + \int^t dt'\; G^i_k(t-t')\, \Xi^k(t') \tag{2.23}$$

where the homogeneous solution $X^i_h(t)$ is independent of the noise, and the propagator G satisfies $G^i_k(0) = \delta^i_k$. In the coincidence limit $t' = t$ we find

$$\frac{\delta X^i(t)}{\delta \Xi^k(t)} = \int^t dt'\; G^i_k(t-t')\,\delta(t-t') = \frac{1}{2}\delta^i_k \tag{2.24}$$

From equations (2.20), (2.22) and (2.24), we get

$$\sigma^{ik} = \Gamma^{ik} + \Gamma^{ki} \tag{2.25}$$

which is the FDT in a simple classical formulation.

In the case of a one-dimensional system, the above argument can be simplified even further because there is only one variable X, and Γ, C, σ are simply constants. In equilibrium, we have $\left\langle X^2 \right\rangle = C^{-1}$. On the other hand, the late time solution of the equations of motion reads

$$X(t) = \int^t du\; e^{-\Gamma C(t-u)}\, \Xi(u) \tag{2.26}$$

which implies $\left\langle X^2 \right\rangle = \sigma/2\Gamma C$. Thus $\sigma = 2\Gamma$, in agreement with equation (2.25).

As an example of this view of the FDT, let us return to the problem of the dissipative pendulum. The system is described by two degrees of freedom x and $p = M\dot{x}$. Since we are interested in the pendulum coming to equilibrium at a given temperature, the relevant thermodynamic potential is $S = -F/k_{\mathrm{B}}T$. We identify the free energy associated with a phase space point (x, p) as the work necessary to bring the pendulum from rest to (x, p), in a reversible way and at constant temperature. This work is, of course, the mechanical energy, so

$$S = -\frac{p^2}{2Mk_{\mathrm{B}}T} - \frac{M\Omega^2 x^2}{2k_{\mathrm{B}}T} \tag{2.27}$$

The forces are then $L_x = M\Omega^2 x/k_{\mathrm{B}}T$ and $L_p = p/Mk_{\mathrm{B}}T$. In these terms, Hamilton's equations become

$$\dot{x} = \frac{p}{M} = k_{\mathrm{B}}TL_p; \qquad \dot{p} = -M\Omega^2 x = -k_{\mathrm{B}}TL_x \tag{2.28}$$

This corresponds to an antisymmetric Γ matrix, and therefore the potential S is conserved. We get no H-theorem, as expected.

In order to obtain regression to equilibrium, we must include dissipation. As is stressed by Landau and Lifshitz, it makes no sense to modify the first of equation (2.28), since this represents the definition of p rather than a true dynamical law. Thus our only possibility is to modify the second equation

$$\dot{p} = -M\Omega^2 x - 2\gamma p = -k_B T\left(L_x + 2M\gamma L_p\right) \tag{2.29}$$

The new understanding is that this modification must be *necessarily* followed by the inclusion of noise $\Xi^i = \left(\tilde{\xi}, \xi\right)$

$$\dot{x} = \frac{p}{M} + \tilde{\xi}; \qquad \dot{p} = -m\omega^2 x - 2\gamma p + \xi \tag{2.30}$$

and that we have no freedom in choosing the noise autocorrelation, as this is given by the FDT. In our case, discarding the antisymmetric part of γ^{ij}, we get $\sigma_{xx} = \sigma_{xp} = 0$, $\sigma_{pp} = 4\gamma Mk_{\mathrm{B}}T$, which of course reproduces the result from the last section.

2.2 The Fokker–Planck and Kramers–Moyal equations

Let us now consider a single variable $X(t)$ evolving according to the Langevin equation [Cha43, Kam81]

$$\frac{dX}{dt}(t) + \Gamma(t)X(t) = \Xi(t) \tag{2.31}$$

(that is, in comparison with equation (2.18), we now take the entropy as simply $S = (-1/2)X^2$, thus $L = X$, and allow Γ to depend on time), where Ξ is a Gaussian *colored* noise

$$\langle \Xi(t)\Xi(t')\rangle = s^2(t, t') \tag{2.32}$$

Under the influence of noise the variable X will show a complicated behavior, even if its initial value is accurately known. It becomes uninteresting to try and follow the evolution of X in all its detail; just knowing the probability density $f\left(x,t\right)$ for actually finding X in a neighborhood of x at times t is enough. Formally

$$f\left(x,t\right)=\left\langle\delta\left(X\left(t\right)-x\right)\right\rangle \tag{2.33}$$

where the average is over realizations of the noise and also over all possible initial conditions $X\left(0\right)$. For simplicity, we assume the noise acts independently of the initial condition.

The probability density f evolves according to the so-called Fokker–Planck equation [Ris89, Gar90]. To derive this equation, observe that [SanMig89]

$$\begin{aligned}\frac{\partial}{\partial t}f\left(x,t\right)&=\left\langle\frac{dX}{dt}\left(t\right)\frac{\partial}{\partial X\left(t\right)}\delta\left(X\left(t\right)-x\right)\right\rangle\\&=-\frac{\partial}{\partial x}\left\langle\frac{dX}{dt}\left(t\right)\delta\left(X\left(t\right)-x\right)\right\rangle\\&=\frac{\partial}{\partial x}\left[\Gamma\left(t\right)xf\left(x,t\right)\right]-\frac{\partial}{\partial x}\left\langle\Xi\left(t\right)\delta\left(X\left(t\right)-x\right)\right\rangle\end{aligned} \tag{2.34}$$

To compute the last expectation value, we appeal to the Novikov identity (2.21)

$$\begin{aligned}\left\langle\Xi\left(t\right)\delta\left(X\left(t\right)-x\right)\right\rangle&=\int_0^t dt'\;s^2\left(t,t'\right)\left\langle\frac{\delta}{\delta\Xi\left(t'\right)}\delta\left(X\left(t\right)-x\right)\right\rangle\\&=-\frac{\partial}{\partial x}\left[\sigma\left(t\right)f\left(x,t\right)\right]\end{aligned} \tag{2.35}$$

where

$$\sigma\left(t\right)=\int_0^t dt'\;s^2\left(t,t'\right)\frac{\delta X\left(t\right)}{\delta\Xi\left(t'\right)} \tag{2.36}$$

which in this simple case can be computed almost explicitly. The final result takes the form of a continuity equation

$$\frac{\partial}{\partial t}f\left(x,t\right)=\frac{\partial}{\partial x}\left\{\left[\Gamma\left(t\right)x+\frac{\partial}{\partial x}\sigma\left(t\right)\right]f\left(x,t\right)\right\} \tag{2.37}$$

One remarkable feature of this equation is that it is *local* in time, in spite of the noise being colored. Moreover, it does not seem possible to reconstruct $s^2\left(t,t'\right)$ from $\sigma\left(t\right)$ in general, unless some further hypothesis is added (for example, that the noise is actually white). In this sense, the original Langevin description contains more information about the system than the Fokker–Planck one [CaRoVe03].

Equation (2.31) may be generalized to nonlinear dynamics [BixZwa71, Zwa73]

$$\frac{dX}{dt}\left(t\right)+\Gamma\left[X\left(t\right),t\right]=\xi\left(t\right) \tag{2.38}$$

Repeating our earlier steps, we find

$$\frac{\partial}{\partial t} f(x,t) = \frac{\partial}{\partial x}\left[\Gamma[x,t] f(x,t)\right] + \frac{\partial^2}{\partial x^2}\int_0^t dt'\ s^2(t,t')\left\langle \frac{\delta X(t)}{\delta \xi(t')}\delta(X(t)-x)\right\rangle \tag{2.39}$$

where

$$\frac{\partial}{\partial t}\frac{\delta X(t)}{\delta \xi(t')} + \frac{\partial \Gamma[X(t),t]}{\partial X(t)}\frac{\delta X(t)}{\delta \xi(t')} = \delta(t-t') \tag{2.40}$$

In general, this will be a complicated function of the base trajectory $X(t)$. However, if the noise is white

$$s^2(t,t') = \sigma^2(t)\,\delta(t-t') \tag{2.41}$$

then the Fokker–Planck equation simplifies to

$$\frac{\partial}{\partial t} f(x,t) = \frac{\partial}{\partial x}\left\{\left[\Gamma[x,t] + \frac{\sigma^2(t)}{2}\frac{\partial}{\partial x}\right] f(x,t)\right\} \tag{2.42}$$

An important particular case of the above is when the Langevin dynamics follows from adding local dissipation and white noise to an otherwise Hamiltonian system. We then have two variables X and P, with

$$\frac{dX}{dt} = \frac{\partial H}{\partial P} \tag{2.43}$$

$$\frac{dP}{dt} = -\frac{\partial H}{\partial X} - 2\gamma P + \xi \tag{2.44}$$

$$H = \frac{P^2}{2M} + V(X) \tag{2.45}$$

where H is the Hamiltonian (following Landau, we only add noise to the second equation). Then

$$f(x,p,t) = \langle \delta(X(t)-x)\,\delta(P(t)-p)\rangle \tag{2.46}$$

and

$$\frac{\partial}{\partial t} f(x,t) = -\{H,f\} + \frac{\partial}{\partial p}\left[\left(2\gamma p + \frac{\sigma^2(t)}{2}\frac{\partial}{\partial p}\right) f\right] \tag{2.47}$$

where

$$\{H,f\} = \frac{\partial H}{\partial p}\frac{\partial f}{\partial x} - \frac{\partial H}{\partial x}\frac{\partial f}{\partial p} \tag{2.48}$$

is the Poisson bracket. This is the so-called Kramers–Moyal equation [Kra40, Moy49].

In the derivation of the Kramers–Moyal equation we have used the fact that a change in the external force changes the acceleration, but neither the position nor the velocity, instantaneously, so

$$\frac{\delta X\left(t\right)}{\delta \xi\left(t\right)}=0 \tag{2.49}$$

The resulting Kramers–Moyal equation contains only second-order p-derivatives. This is the so-called *normal* diffusion. For colored noise there are both normal and anomalous diffusion (we shall see an example in Chapter 3).

For a thermodynamic system in contact with a heat bath any spontaneous transformation decreases the free energy $F=U-TS$. For a system described by the Kramers–Moyal equation, if both γ and σ^2 are time-independent, there is an analog to this statement. We replace the internal energy U by the average value of the Hamiltonian, the entropy S by the Boltzmann H_{B} function

$$H_{\mathrm{B}}=-k_{\mathrm{B}}\int dXdP\ f\ln\left[f\right] \tag{2.50}$$

and the temperature T by $\sigma^2/4M\gamma k_{\mathrm{B}}$ [cf. equation (2.7)]. Thus we obtain Kramers' nonequilibrium free energy [Kur98, Kur05]

$$F_K=\int dXdP\ f\left\{H+\frac{\sigma^2}{4M\gamma}\ln\left[f\right]\right\} \tag{2.51}$$

and an H-theorem of sorts

$$\frac{dF_K}{dt}=-\frac{2\gamma}{M}\int dXdP\ f\left[P+\frac{\sigma^2\left(t\right)}{4\gamma f}\frac{\partial f}{\partial P}\right]^2 \tag{2.52}$$

This also shows that there is only one stationary solution

$$f_{\mathrm{eq}}\propto e^{-\left(4\gamma M/\sigma^2\right)H} \tag{2.53}$$

so we are led to the identify $\sigma^2=4\gamma Mk_{\mathrm{B}}T$, as expected.

If γ and σ^2 go to zero, the Kramers–Moyal equation reduces to the Liouville equation

$$\frac{\partial}{\partial t}f\left(x,t\right)=-\left\{H,f\right\} \tag{2.54}$$

In the opposite limit, it reduces to a Fokker–Planck equation. For very large damping, we have

$$P\sim\frac{1}{2\gamma}\left[-V'+\xi\right] \tag{2.55}$$

$$\frac{dX}{dt}=-\frac{V'\left(X\right)}{2\gamma M}+\Xi\sim-\frac{V''\left(0\right)}{2\gamma M}X+\Xi \tag{2.56}$$

where $\Xi=\xi/2\gamma M$. This is the kind of dynamics we studied at the beginning of this section. Since the kinetic energy is negligible compared to the potential energy, we have $S=-V\left(X\right)/k_{\mathrm{B}}T$, $C=V''\left(0\right)/k_{\mathrm{B}}T$ and $\Gamma=k_{\mathrm{B}}T/2\gamma M$.

The fluctuation–dissipation relation appropriate to the Fokker–Planck equation $\langle \Xi(t)\,\Xi(t')\rangle = 2\Gamma\delta(t-t')$ leads us back to $\langle \xi(t)\,\xi(t')\rangle = 4\gamma M k_{\mathrm{B}} T\delta(t-t')$.

2.3 The Boltzmann equation

We shall now examine the other major paradigm of irreversible behavior in classical physics, namely, Boltzmann's theory of dilute gases [Bol64, ChaCow39, LifPit81]. As we already mentioned, the Brownian motion paradigm we examined in the last section corresponds to an *autocratic* system where an environment is subservient to our system of interest. The Boltzmann model of a gas, on the other hand, seems to be *democratic* in that it embraces all molecules on equal terms. In this sense, the Boltzmann gas appears as a truly closed system. However, this system will be shown to be an effectively open system in the space of correlation functions. Specifically, our relevant system shall be the one-particle distribution function, and its environment consists of the higher correlations. When seen in this light, we shall see that irreversibility in the Boltzmann equation follows a similar pattern as in the Brownian motion problem.

This view of the Boltzmann theory as describing an effectively open system shows how nontrivial it may be to identify the right degrees of freedom to describe a given system. We may say that the genius of Boltzmann has been to realize that, while the characteristic time for the dynamics of individual molecules is the collision time, the characteristic time for the dynamics of the one-particle distribution function is the relaxation time, which is much longer. Thus, the one-particle distribution function is the collective degrees of freedom in whose terms the dynamics becomes slow and simple. The very first step in treating the nonequilibrium dynamics of a system, i.e. identifying the right collective degrees of freedom in a given situation, may turn out to be the most important, and at times the most difficult, task.

Consider a gas of N identical molecules interacting through a binary central potential $V(r)$; we shall assume the forces are short range and the gas is dilute, $Na^3/V \ll 1$ where a is the range of the potential. We shall consider no external forces. The Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} V_{ij}; \qquad V_{ij} = V(|\mathbf{x}_i - \mathbf{x}_j|) \tag{2.57}$$

(we assume no self-energies: $V_{ii} = 0$) leads to the Hamilton equations

$$\frac{d\mathbf{x}^i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}^i}{m}; \qquad \frac{d\mathbf{p}^i}{dt} = -\frac{\partial H}{\partial \mathbf{x}_i} = -\sum_{i\neq j} \frac{\partial V_{ij}}{\partial \mathbf{x}_i} \tag{2.58}$$

Equivalently we may describe the state of the system through a $6N$-dimensional distribution function $\rho = \rho((\mathbf{x}_1, \mathbf{p}_1), \ldots, (\mathbf{x}_N, \mathbf{p}_N), t)$, which satisfies the

Liouville equation

$$\frac{\partial \rho}{\partial t} = -\left\{H, \rho\right\} \tag{2.59}$$

where we introduced the Poisson bracket (generalizing (2.48))

$$\left\{f, g\right\} = \sum_{i=1}^{N}\left[\frac{\partial f}{\partial \mathbf{p}_i}\frac{\partial g}{\partial \mathbf{x}_i} - \frac{\partial g}{\partial \mathbf{p}_i}\frac{\partial f}{\partial \mathbf{x}_i}\right] \tag{2.60}$$

ρ integrates to 1 over the whole phase space. We shall assume that ρ is totally symmetric, which in the quantum case yields Bose–Einstein statistics.

Given a (one-particle) phase space point $(\mathbf{x}, \mathbf{p})$, we may define the density at that point

$$\mathcal{F}\left(\mathbf{x}, \mathbf{p}\right) = \sum_{i=1}^{N} \delta\left(\mathbf{x}_i - \mathbf{x}\right)\delta\left(\mathbf{p}_i - \mathbf{p}\right) \tag{2.61}$$

The one-particle distribution function f_1 is the expectation value of the density

$$f_1\left(\mathbf{x}, \mathbf{p}\right) = \sum_{i=1}^{N} \left\langle \delta\left(\mathbf{x}_i - \mathbf{x}\right)\delta\left(\mathbf{p}_i - \mathbf{p}\right)\right\rangle \tag{2.62}$$

$$\begin{aligned}&\left\langle \delta\left(\mathbf{x}_i - \mathbf{x}\right)\delta\left(\mathbf{p}_i - \mathbf{p}\right)\right\rangle \\ &\quad = \int \prod_{j} d^3\mathbf{x}_j d^3\mathbf{p}_j \; \rho\left(\left(\mathbf{x}_1, \mathbf{p}_1\right), \ldots, \left(\mathbf{x}_N, \mathbf{p}_N\right), t\right)\delta\left(\mathbf{x}_i - \mathbf{x}\right)\delta\left(\mathbf{p}_i - \mathbf{p}\right)\end{aligned} \tag{2.63}$$

which from symmetry becomes

$$\left\langle \delta\left(\mathbf{x}_i - \mathbf{x}\right)\delta\left(\mathbf{p}_i - \mathbf{p}\right)\right\rangle = \int \prod_{j=2}^{N} d^3\mathbf{x}_j d^3\mathbf{p}_j \; \rho((\mathbf{x}, \mathbf{p}), (\mathbf{x}_2, \mathbf{p}_2), \ldots, (\mathbf{x}_N, \mathbf{p}_N), t) \tag{2.64}$$

and is independent of i. Therefore

$$f_1\left(\mathbf{x}, \mathbf{p}\right) = N \int \prod_{j=2}^{N} d^3\mathbf{x}_j d^3\mathbf{p}_j \; \rho((\mathbf{x}, \mathbf{p}), (\mathbf{x}_2, \mathbf{p}_2), \ldots, (\mathbf{x}_N, \mathbf{p}_N), t) \tag{2.65}$$

For later use, we shall introduce also the s-particle distribution function

$$\begin{aligned}&f_s\left(\left(\mathbf{x}_1, \mathbf{p}_1\right), \ldots, \left(\mathbf{x}_s, \mathbf{p}_s\right)\right) \\ &\quad = \frac{N!}{(N-s)!}\int \prod_{j=s+1}^{N} d^3\mathbf{x}_j d^3\mathbf{p}_j \; \rho((\mathbf{x}_1, \mathbf{p}_1), \ldots, (\mathbf{x}_s, \mathbf{p}_s), (\mathbf{x}_{s+1}, \mathbf{p}_{s+1}) \ldots)\end{aligned} \tag{2.66}$$

We obtain the dynamics of f_1 integrating side by side in Liouville's equation

$$\frac{\partial f_1}{\partial t} = -N \int \prod_{j=2}^{N} d^3\mathbf{x}_j d^3\mathbf{p}_j \; \left\{H, \rho\right\} \tag{2.67}$$

Developing the Poisson bracket, we observe that all terms involving derivatives with respect to $\mathbf{x}_j$ or $\mathbf{p}_j$, $j \neq 1$, may be reduced to total derivatives and discarded (under suitable boundary conditions at infinity). The only surviving terms yield

$$\frac{\partial f_1}{\partial t}(\mathbf{x}_1, \mathbf{p}_1) = -\frac{\mathbf{p}_1}{m}\frac{\partial f_1}{\partial \mathbf{x}_1} + \frac{\partial}{\partial \mathbf{p}_1}\int d^3\mathbf{x}_2 d^3\mathbf{p}_2 \left[\frac{\partial}{\partial \mathbf{x}_1} V(|\mathbf{x}_1 - \mathbf{x}_2|)\right] \times f_2((\mathbf{x}_1, \mathbf{p}_1), (\mathbf{x}_2, \mathbf{p}_2)) \tag{2.68}$$

To obtain the dynamics for f_1 we need the dynamics for f_2. This is obtained in an analogous way

$$\frac{\partial f_2}{\partial t} = -N(N-1)\int \prod_{j=3}^{N} d^3\mathbf{x}_j d^3\mathbf{p}_j \ \{H, \rho\} \tag{2.69}$$

Repeating the above argument, we get

$$\frac{\partial f_2}{\partial t} = -\{H_2, f_2\} + \int d^3\mathbf{x}_3 d^3\mathbf{p}_3 \ K f_3 \tag{2.70}$$

where H_2 is the two-particle Hamiltonian

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + V(|\mathbf{x}_1 - \mathbf{x}_2|) \tag{2.71}$$

The precise form of the kernel K in equation (2.70) is unimportant. What matters is that, if the dynamics of f_1 depends on f_2, it will depend on f_3, which in turn depends on f_4, etc. Thus we obtain an infinite hierarchy of equations, commonly known as the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy.

We face a situation which is different from our oversimplified Brownian motion model. In the linearly coupled harmonic oscillators problem the dynamics is so simple that one is seriously tempted to just solve it, without ever mobilizing all the Langevin equation machinery. In the BBGKY case, a solution of the infinite hierarchy is close to impossible. So we need to find ways to reduce the problem to a simpler one. Usually the first step in this simplification is to reduce the infinite hierarchy to a finite system by just discarding an infinite set of distribution functions. We shall call this brute force reduction a *truncation* of the hierarchy.

For example, we may argue that, since the integral over $\mathbf{x}_2$ is effectively reduced to a sphere of radius a around $\mathbf{x}_1$, the collision term in equation (2.68) is smaller than the first term by a factor Na^3/V, which is $\ll 1$ by assumption. In turn, the collision term in equation (2.70) will be smaller than the other terms in this equation by about the same factor. For a dilute gas with short-range interactions, we would be dealing with small corrections to ever smaller terms, and at some point they may become negligible. For simplicity, we shall assume that we are interested in a situation where the first nontrivial truncation works, namely, we put $K = 0$ in equation (2.70).

We stress that this strategy is by no means guaranteed to work. If there were long-range interactions (like Coulomb forces), something drastically different may be required, such as a Vlasov scheme where all far away particles are replaced by an effective continuous charge distribution supporting an average potential. This is another example of why finding the right collective degrees of freedom may constitute the hardest part of the work, as we already mentioned.

2.3.1 Slaving of higher correlations in the Boltzmann equation

Our goal is to solve equation (2.70) for f_2 (with $K = 0$) and to substitute the solution in equation (2.68) for f_1. At first sight it may look like these equations are decoupled, but, as we shall see, they couple through the boundary conditions, as the behavior of f_2 for large separations will be determined by f_1, through the so-called *molecular chaos* hypothesis [AkhPel81].

Equation (2.70) expresses the conservation of probability as the particles move along the classical orbits generated by the Hamiltonian H_2. These trajectories are easiest to study if we decompose the motion in center of mass and relative variables

$$\mathbf{X} = \frac{1}{2}(\mathbf{x}_1 + \mathbf{x}_2); \qquad \mathbf{u} = \mathbf{x}_1 - \mathbf{x}_2 \tag{2.72}$$

Introducing the conjugate momenta

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2; \qquad 2\mathbf{p} = \mathbf{p}_1 - \mathbf{p}_2 \tag{2.73}$$

we get the Hamiltonian

$$H_2 = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + V(u); \qquad M = 2m,\ \mu = \frac{m}{2} \tag{2.74}$$

The center of mass motion represents a particle of mass M moving with uniform speed, while the relative motion represents a particle of mass μ scattering off a fixed center of force at the origin.

Let us observe that the integral in equation (2.68) is effectively restricted to the range $|\mathbf{x}_1 - \mathbf{x}_2| \sim a$, and so the center of mass variable changes little. Thus we may ignore the dependence of f_2 on X (on a more formal level, we are computing the first term in a development of the collision integral in derivatives with respect to X). Also an initial domain of initial conditions will move along the classical orbits and be distorted. Since relative motion is very fast with respect to macroscopic time-scales, we may assume that on the time-scales relevant to our observations, the initial domain has been elongated and fills the classical trajectory uniformly (this effect is known as phase diffusion, or the running men effect: a line of runners with differential velocities will elongate and eventually go uniformly round the track). Under the twin hypothesis of center of mass independence and phase diffused relative motion, we get $f_{2,t} = f_{2,\mathbf{X}} = 0$, and the equation for f_2 becomes

$$\frac{\mathbf{p}}{\mu} \cdot \nabla_{\mathbf{u}} f_2 - (\nabla_{\mathbf{u}} V) \cdot \nabla_{\mathbf{p}} f_2 = 0 \tag{2.75}$$

We may add a term

$$[\nabla_{\mathbf{x}_2} V(|\mathbf{x}_1 - \mathbf{x}_2|)]\, \nabla_{\mathbf{p}_2} f_2\left((\mathbf{x}_1, \mathbf{p}_1), (\mathbf{x}_2, \mathbf{p}_2)\right) \tag{2.76}$$

under the integral in equation (2.68), since it integrates to zero anyway. Now observe that

$$\nabla_{\mathbf{x}_1} V(|\mathbf{x}_1 - \mathbf{x}_2|) = -\nabla_{\mathbf{x}_2} V(|\mathbf{x}_1 - \mathbf{x}_2|) = \nabla_{\mathbf{u}} V \tag{2.77}$$

$$\nabla_{\mathbf{p}_1} f_2 - \nabla_{\mathbf{p}_2} f_2 = \nabla_{\mathbf{p}} f_2 \tag{2.78}$$

Changing variables from $\mathbf{x}_2$ to $\mathbf{u}$, we get

$$\frac{\partial f_1}{\partial t}(\mathbf{x}_1, \mathbf{p}_1) = -\frac{\mathbf{p}_1}{m} \nabla_{\mathbf{x}_1} f_1 + \int d^3\mathbf{p}_2 \int d\mathbf{u}\, \frac{\mathbf{p}}{\mu} \nabla_{\mathbf{u}} f_2 \tag{2.79}$$

For a given $\mathbf{p}$, we may choose adapted cylindrical coordinates (u, b, φ). Then this simplifies to

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m} \frac{\partial f_1}{\partial \mathbf{x}_1} = \int d^3\mathbf{p}_2 \int 2\pi b db\, \frac{|\mathbf{p}|}{\mu} [f_2(\mathbf{p}_1, \mathbf{p}_2, b, u = \infty) \\ - f_2(\mathbf{p}_1, \mathbf{p}_2, b, u = -\infty)] \tag{2.80}$$

where by $u = \pm\infty$ we mean a relative coordinate which is large enough to take the particles out of interaction range, but still small in macroscopic terms.

It is at this point that the crucial step is taken. At $u = -\infty$, the two particles have not yet interacted. Here we impose the molecular chaos condition, namely, that there are no correlations among them initially, and thus

$$f_2(\mathbf{p}_1, \mathbf{p}_2, b, u = -\infty) \sim f_1(\mathbf{x}_1, \mathbf{p}_1)\, f_1(\mathbf{x}_1, \mathbf{p}_2) \tag{2.81}$$

At $u = \infty$ the particles have interacted and are correlated. However, since f_2 is constant along the trajectories, we have

$$f_2(\mathbf{p}_1, \mathbf{p}_2, b, u = \infty) = f_2(\mathbf{p}'_1, \mathbf{p}'_2, b, u = -\infty) \sim f_1(\mathbf{x}_1, \mathbf{p}'_1)\, f_1(\mathbf{x}_1, \mathbf{p}'_2) \tag{2.82}$$

where $\mathbf{p}'_1, \mathbf{p}'_2$ are the momenta which evolve into $\mathbf{p}_1, \mathbf{p}_2$ after a collision with impact parameter b. Equations (2.81) and (2.82) implement the *slaving* of the two-particle correlation to the one-particle distribution. After this, no trace of f_2 is left, but only functionals of f_1.

To make the content of these equations even clearer, let us write

$$f_2(\mathbf{p}_1, \mathbf{p}_2, b, u = \infty) = \int d^3\mathbf{p}_3 d\mathbf{p}_4\, \delta(\mathbf{p}_3 - \mathbf{p}'_1)\, \delta(\mathbf{p}_4 - \mathbf{p}'_2)\, f_1(\mathbf{x}_1, \mathbf{p}_3)\, f_1(\mathbf{x}_1, \mathbf{p}_4) \tag{2.83}$$

and also the trivial identity

$$f_2(\mathbf{p}_1, \mathbf{p}_2, b, u = -\infty) = \int d^3\mathbf{p}_3 d\mathbf{p}_4\, \delta(\mathbf{p}_3 - \mathbf{p}'_1)\, \delta(\mathbf{p}_4 - \mathbf{p}'_2)\, f_1(\mathbf{x}_1, \mathbf{p}_1)\, f_1(\mathbf{x}_1, \mathbf{p}_2) \tag{2.84}$$

The final result is

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m}\frac{\partial f_1}{\partial \mathbf{x}_1} = \int d^3\mathbf{p}_2 d^3\mathbf{p}_3 d^3\mathbf{p}_4 \, \mathbf{T}\left(\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \mathbf{p}_4\right) \times \left\{f_1\left(\mathbf{p}_3\right) f_1\left(\mathbf{p}_4\right) - f_1\left(\mathbf{p}_1\right) f_1\left(\mathbf{p}_2\right)\right\} \tag{2.85}$$

where $\mathbf{T}$ is the transition probability

$$\mathbf{T} = \int 2\pi b db \, \frac{|\mathbf{p}|}{\mu} \delta\left(\mathbf{p}_3 - \mathbf{p}_1'\right) \delta\left(\mathbf{p}_4 - \mathbf{p}_2'\right) \tag{2.86}$$

$\mathbf{T}$ is zero unless $\mathbf{p}_3, \mathbf{p}_4$ do evolve into $\mathbf{p}_1, \mathbf{p}_2$ for *some* impact parameter. Equation (2.85) is the Boltzmann equation, and it is dissipative. We observe that the source of dissipation is the slaving of f_2 to f_1, similar in philosophy as in our Brownian motion toy model. As in Brownian motion, in equilibrium there will be density fluctuations. Thus equation (2.85) is incomplete: there must also be a stochastic term, which is determined by the fluctuation–dissipation theorem. We shall derive this term, but first let us consider the changes in equation (2.85) brought by relativity and quantum statistics.

2.3.2 Corrections from quantum statistics

The Boltzmann equation has the structure of a balance equation where changes in the particle number within a given cell in phase space are attributed (other than transport along classical one-particle trajectories) either to gain or loss processes. Gain obtains when one of two particles with momenta p_3, p_4 are injected into the cell through a collision, and loss when a particle within the cell is scattered off by collision with another particle of momentum p_2. If the particles obey quantum statistics, we must take into account the effect of stimulated emission for Bose–Einstein (BE) statistics and Pauli blocking for Fermi–Dirac (FD) statistics [Lib98]. The kinetic equation is then changed into

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m}\frac{\partial f_1}{\partial \mathbf{x}_1} = \int d^3\mathbf{p}_2 d^3\mathbf{p}_3 d^3\mathbf{p}_4 \, \mathbf{T} \, \mathbf{I} \tag{2.87}$$

where $\mathbf{T}$ is a suitable transition probability, not necessarily identical to (2.86), and

$$\mathbf{I} = \left(1 \pm f_1\right)\left(1 \pm f_2\right) f_3 f_4 - \left(1 \pm f_3\right)\left(1 \pm f_4\right) f_1 f_2 \tag{2.88}$$

Hereafter we drop the subindex 1 in f (we shall not consider higher correlation functions) and use the shorthand $f_i = f\left(\mathbf{x}, \mathbf{p}_i\right)$. The upper sign holds for BE, and the lower sign for FD.

In equilibrium the collision integral must vanish, and therefore $\ln\left[f/(1 \pm f)\right]$ must be an additive constant of motion [Hua87]. If the gas is globally at rest, we may discard a term proportional to $\mathbf{p}$, which would conflict with rotational invariance, to get

$$\ln\frac{f}{1 \pm f} = -\beta\left(\varepsilon - \mu\right) \tag{2.89}$$

where ε is the one-particle energy, and β and μ are constants. Therefore

$$f_{eq} = \frac{1}{e^{\beta(\varepsilon-\mu)} \mp 1} \tag{2.90}$$

where again the signs correspond to BE (upper) or FD (lower) statistics. We recognize that $\beta = 1/k_{\mathrm{B}}T$, and μ is the chemical potential. From now on we shall assume BE statistics.

The lesson from equation (2.90) is that to specify an equilibrium state we need five numbers: the three components of the velocity of the rest frame, and the temperature and chemical potential in that frame. In other words, equilibrium states are astonishingly simpler than the generic states of the theory, which live in a $6N$-dimensional parameter space. This essential simplicity is the ultimate reason why we can describe real physical systems so elegantly by thermodynamics and statistical mechanics.

2.3.3 Relativistic kinetic theory

Let us now add the demands of relativity [Isr72, Isr88]. We consider our particles as living in a four-dimensional spacetime with coordinates x^μ ($x^0 = ct$, $x^i = x, y, z$), endowed with a metric tensor $g_{\mu\nu}$, which in Minkowski space is just $\eta_{\mu\nu} = \mathrm{diag}\,(-1, 1, 1, 1)$ (we use Misner–Thorne–Wheeler conventions (MTW) [MiThWh72]). The system is described by the one-particle distribution function $f\,(x^\mu, p_\mu)$, where x is a position variable, and p is a momentum variable. Momentum is assumed to lie on a mass shell $p^2 + M^2 = 0$ and have positive energy $p^0 > 0$.

We assume there is a conserved charge which allows us to define a meaningful conserved particle number. Given a spatial element $d\Sigma^\mu = n^\mu d\Sigma$ and a momentum space element d^4p, the number of particles with momentum p lying within that phase space volume element is

$$dn = -4\pi f\,(x, p)\, \theta\left(p^0\right) \delta\left(p^2 + M^2\right) p^\mu n_\mu \, d\Sigma \frac{d^4p}{(2\pi)^4 \sqrt{-g}} \tag{2.91}$$

where the normalization will be useful later on. In this formula, $g = \det g_{\mu\nu}$; of course, $-g = 1$ in Minkowski space, which we shall assume from now on. Observe that this definition is covariant. The particle number *density* is defined as (minus) the flux of the particle number *current*

$$N^\mu\,(x) = 2 \int Dp\; p^\mu f\,(x, p) \tag{2.92}$$

where we introduced the momentum space volume element

$$Dp = \theta\left(p^0\right) \delta\left(p^2 + M^2\right) \frac{d^4p}{(2\pi)^3 \sqrt{-g}} \tag{2.93}$$

If we are only concerned with the particle number flux across equal time surfaces, we may decompose the particle current into $N^\mu = (c\rho, \mathbf{J})$, where ρ is the ordinary density and $\mathbf{J}$ the ordinary particle flux.

The energy–momentum density is defined in terms of the energy–momentum *tensor*

$$dP^\mu = -T^{\mu\nu} d\Sigma_\nu; \qquad T^{\mu\nu} = 2\int Dp\, p^\mu p^\nu f(x,p) \tag{2.94}$$

$T^{00} = cE$, where E is the ordinary energy density, $T^{0i} = \mathbf{E}$ are the energy flux, $T^{i0} = c\mathbf{P}$ are the momentum density, and T^{ij} are the components of the momentum flux. Since $T^{\mu\nu}$ is symmetric, we get $\mathbf{P} = \mathbf{E}/c$.

The dynamics of the distribution function is given by the Boltzmann equation

$$p_1^\mu \frac{\partial}{\partial x^\mu} f = I_{\text{col}} \tag{2.95}$$

$$I_{\text{col}} = \int \left[\prod_{i=2}^{4} Dp_i\right] \left[(2\pi)^4 \delta(p_1 + p_2 - p_3 - p_4)\right] \mathbf{T}\,\mathbf{I} \tag{2.96}$$

where once again $\mathbf{T}$ is a suitable transition probability, not necessarily identical to (2.86), and $\mathbf{I}$ is given in equation (2.88). We have made explicit the momentum conservation delta function, and assume that the transition probability $\mathbf{T}$ is symmetric under particle exchange and time reversal. These symmetry conditions lead directly to the conservation laws for particle number and energy–momentum $N^\mu_{;\mu} = T^{\mu\nu}_{;\nu} = 0$, which hold for *any* distribution function. In equilibrium, we have the stronger result $\mathbf{I} = 0$, leading to

$$f_{\text{eq}} = \frac{1}{e^{-\beta_\mu p^\mu - \alpha} - 1}, \tag{2.97}$$

where $\beta^\mu = \mu^\mu / k_{\text{B}}T$, u^μ is the macroscopic four-velocity of the gas $(u^2 = -1)$ and $\alpha = \mu / k_{\text{B}}T$. The number of parameters which identify an equilibrium state remains at five.

Besides the conserved currents N^μ and $T^{\mu\nu}$, we may define the entropy current

$$S^\mu(x) = \int Dp\, p^\mu \left\{[1 + f(p)] \ln[1 + f(p)] - f(p) \ln f(p)\right\} \tag{2.98}$$

Unlike the other currents, entropy is not conserved: $S^\mu_{;\mu} \geq 0$ is the relativistic H-theorem.

Consider a small deviation from the equilibrium distribution $f = f_{\text{eq}} + \delta f$ corresponding to the same particle and energy fluxes

$$\int Dp\, p^\mu \delta f(p) = \int Dp\, p^\mu p^0 \delta f(p) = 0 \tag{2.99}$$

The variation in entropy becomes

$$\delta S^0 = -\frac{1}{2}\int Dp\, p^0 \frac{(\delta f)^2}{[1 + f_{\text{eq}}(p)]\, f_{\text{eq}}(p)} \tag{2.100}$$

showing that entropy is indeed a maximum at equilibrium.

In the classical theory, the distribution function is concentrated on the positive frequency mass shell. Therefore, it is convenient to label momenta just by their spatial components $\mathbf{p}$, the temporal component being necessarily $\omega_p = \sqrt{M^2 + \mathbf{p}^2} > 0$. In the same way, it is simplest to regard the distribution function as a function of the three momentum $\mathbf{p}$ alone, according to the rule

$$f^{(3)}\left(x, \mathbf{p}\right) = f\left[x, \left(\omega_p, \mathbf{p}\right)\right] \tag{2.101}$$

where f represents the distribution function as a function on four-dimensional momentum space, and $f^{(3)}$ its restriction to the three-dimensional mass shell. With this understood, we shall henceforth drop the superscript, using the same symbol f for both functions, since only the distribution function on mass shell enters into our discussion. The variation of the total entropy now reads

$$\delta S = -\frac{1}{2}\int d^3\mathbf{x} \int \frac{d^3\mathbf{p}}{(2\pi)^3}\frac{(\delta f)^2}{\left[1 + f_{\mathrm{eq}}\left(p\right)\right] f_{\mathrm{eq}}\left(p\right)} \tag{2.102}$$

This formula shall be relevant to our discussion of fluctuations in the Boltzmann equation.

2.3.4 Fluctuations in the Boltzmann equation

We have seen that the Boltzmann equation has a dissipative character: by virtue of the H-theorem, *any* initial condition is eventually transformed into the equilibrium solution. On the other hand, we have seen that there is a well-defined entropy decrease associated with fluctuations in the distribution function. If we believe in Einstein's formula for the probability of a fluctuation, we must conclude that in equilibrium the number of particles in a phase space cell must not have a definite value, but rather be a Gaussian stochastic variable with mean deviation

$$\left\langle \delta f\left(\mathbf{x}, \mathbf{p}\right) \delta f\left(\mathbf{x}', \mathbf{p}'\right)\right\rangle \sim (2\pi)^3\, \delta\left(\mathbf{x} - \mathbf{x}'\right) \delta\left(\mathbf{p} - \mathbf{p}'\right) f_{\mathrm{eq}}\left[1 + f_{\mathrm{eq}}\right] \tag{2.103}$$

It is not hard to derive this result. The formula for the equilibrium distribution function is equivalent to considering the gas in a grand canonical ensemble, and therefore there must be number fluctuations

$$\left\langle (\delta N)^2 \right\rangle = \beta \frac{\partial \left\langle N \right\rangle}{\partial \mu} = \int d^3\mathbf{x} \frac{d^3\mathbf{p}}{(2\pi)^3}\; f_{\mathrm{eq}}\left[1 + f_{\mathrm{eq}}\right] \tag{2.104}$$

On the other hand

$$N = \int d^3\mathbf{x} \frac{d^3\mathbf{p}}{(2\pi)^3}\; f \tag{2.105}$$

so

$$\left\langle (\delta N)^2 \right\rangle = \int d^3\mathbf{x} \frac{d^3\mathbf{p}}{(2\pi)^3} d^3\mathbf{x}' \frac{d^3\mathbf{p}'}{(2\pi)^3}\; \left\langle \delta f\left(\mathbf{x}, \mathbf{p}\right) \delta f\left(\mathbf{x}', \mathbf{p}'\right)\right\rangle \tag{2.106}$$

taking us back to equation (2.103). This means that if at $t = 0$ we actually measure the number of particles f_0 in each phase space cell, we will rarely obtain those given by f_{eq} (although we will get numbers that will remain statistically close to it). However, if we adopt f_0 as the initial condition and solve the Boltzmann equation, after a long enough time the solution converges to f_{eq} in each and every cell. To obtain these occupation numbers from an actual measurement would be highly unlikely for a system in equilibrium under a grand canonical distribution.

This outrage against Gibbsian common sense means that the Boltzmann equation is not telling the whole story. There is another term besides the collision integral, which sustains the right amount of deviations from the equilibrium state. We could trace back to the derivation of the Boltzmann equation to see where the relevant information was disregarded (and for this reason, we unfolded that derivation in some detail). However, in practice, we know this extra term represents fluctuations which may be quantified by a noise distribution, whose statistics is determined from fluctuation–dissipation considerations; for some classic implementations of this insight see [LanLif57, LanLif59, FoxUhl70a, FoxUhl70b, BixZwa69, KacLog76, KacLog79]. The two points we wish to stress are (1) the incompleteness of the Boltzmann equation which only accounts for dissipation, and (2) the possibility of using fluctuation–dissipation relation considerations to add fluctuations to the Boltzmann equation, valid *for all practical purposes.*

Let us consider the regression of a small deviation δf from the equilibrium distribution f_{eq}. In order to apply the fluctuation–dissipation theorem we must obtain an expression for the time derivative of δf in terms of the thermodynamic force

$$F(x,\mathbf{p}) = -\frac{\delta S}{\delta(\delta f)} = \frac{1}{(2\pi)^3}\frac{\delta f(x,\mathbf{p})}{[1+f_{\mathrm{eq}}(p)]\,f_{\mathrm{eq}}(p)} \tag{2.107}$$

Writing the linearized equation as

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{\omega_p}\nabla f = \frac{1}{\omega_p} I_{\mathrm{col}} + \xi(X,\mathbf{p}) \tag{2.108}$$

the Γ matrix has an asymmetric part (coming from the spatial gradients term) and a symmetric part (coming from the linearization of the collision integral). Only the latter contributes to the noise autocorrelation, and so we obtain

$$\langle \xi(X,\mathbf{p})\,\xi(Y,\mathbf{q})\rangle = -\left\{\frac{1}{\omega_p}\frac{\delta I_{\mathrm{col}}(X,\mathbf{p})}{\delta F(Y,\mathbf{q})} + \frac{1}{\omega_q}\frac{\delta I_{\mathrm{col}}(Y,\mathbf{q})}{\delta F(X,\mathbf{p})}\right\} \tag{2.109}$$

To obtain a crude idea of what is going on, we may keep only those terms in I_{col} which are proportional to $F(\mathbf{p})$, as is usually done in deriving the “collision time approximation” to the Boltzmann equation (also related to the Krook–Bhatnager–Gross kinetic equation [Lib98, Cer69]), thus we write

$$\delta I_{\mathrm{col}}(\mathbf{p}) \sim -\omega_p \nu^2(\mathbf{p}) F(x,\mathbf{p}) \tag{2.110}$$

where

$$\nu^2(X,\mathbf{p}) = \frac{(2\pi)^3}{\omega_p}\int\left[\prod_{i=2}^{4} Dp_i\right]\left[(2\pi)^4\,\delta\left(p_1+p_2-p_3-p_4\right)\right]\mathbf{T}I_+ \tag{2.111}$$

$$I_+ = \left[1+f_{\mathrm{eq}}\left(p_1\right)\right]\left[1+f_{\mathrm{eq}}\left(p_2\right)\right]f_{\mathrm{eq}}\left(p_3\right)f_{\mathrm{eq}}\left(p_4\right) \tag{2.112}$$

Under this approximation we find the noise autocorrelation

$$\langle\xi(y,\mathbf{k})\xi\left(x,\mathbf{p}\right)\rangle = 2\delta^{(4)}\left(x-y\right)\delta\left(\mathbf{k}-\mathbf{p}\right)\nu^2(x,\mathbf{p}) \tag{2.113}$$

Equations (2.108) and (2.113) are the solution to our problem, that is, they describe the fluctuations in the Boltzmann equation, required by consistency with the FDT. Observe that, unlike equation (2.103), the mean square value of the stochastic force vanishes for a free gas. This does not mean that there are no fluctuations (equation (2.103) does not vanish) but that in the collisionless case it is enough to include the fluctuations in the initial conditions, since they are preserved by the dynamics. It is only in the dissipative case that an explicit noise term is necessary to keep fluctuations at the required level [CalHu00].