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Statistical Thermodynamics and Stochastic Theory of Nonequilibrium Systems

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Chapter 5

Fluctuations and Linear Irreversible Processes

5.1 Einstein's theory of fluctuations

In this chapter we will present several aspects of the statistical theory of fluctuations and the theory of linear irreversible processes (Haase, 1963; Prigogine, 1967, Keller, 1977; DeGroot & Mazur, 1984, Schwabl, 2000, Schimansky-Geier & Talkner, 2002). This theory is a well developed part of the statistical physics which holds true close to equilibrium. The main result of the statistical theory near to equilibrium is the foundation of a deep connection between fluctuations and dissipation, both phenomena seemingly not related one to the other. This insight is due mainly to the work of Einstein and Onsager. One of our main topics is the study of the interaction of the degree of freedom under consideration with the surrounding. In this relation the concrete way of interaction with the particles or dynamic modes of the surrounding is not of interest for the description of

the relevant variables. This interaction causes dissipation, i.e. the distribution of concentrated energy to many degrees of freedom and causes deviations from the equilibrium states, fluctuations. Thus as will be shown, the correlation functions and spectra of the fluctuations stand in close relation to the response function on external forces, to the dissipative and transport coefficients as long as the linear approximation around an equilibrium states holds. Unfortunately the extension of this beautiful theory to all systems far from equilibrium is impossible.

The *Boltzmann-Planck principle* developed in Section 4.1 was generalized by Einstein and applied to fluctuations in several seminal papers published in 1902-1906. Suppose that x should be a fluctuating quantity of a thermodynamic system. Taking the general view of statistical physics, we will assume that x is an explicit function of the microscopic variables.

$$x = x(q_1, ..., p_f). \tag{5.1}$$

Suppose further on that we deal with an isolated thermodynamic system, i.e. E, N, V are (macroscopic) constants. We want to find the probability distribution $w(x)$ of the fluctuating value x under the

given isoenergetic conditions. The key for the solution of this problem is the statistical definition of the thermodynamic entropy due to Boltzmann and Planck (see Section 4.1). Under the assumption of thermodynamic equilibrium at fixed E, V, N we will introduce a conditional entropy $S(x|E, V, N)$ for the microscopic states where a certain value of x is realized. Geometrically the form $x = const$ is some subset of the hypersurface $E = const.$. Therefore, this entropy is determined by the number of microscopic states or in other words by the thermodynamic weight $\Omega(x|E, V, N)$ of the states which correspond to the value of x:

$$S(x|E, V, N) = k_B \ln \Omega(x|E, V, N). \tag{5.2}$$

The probability distribution to find a certain value of x is then defined by

$$\omega(x|E, V, N) = \frac{\Omega(x|E, V, N)}{\Omega(E, V, N)} \tag{5.3}$$

or respectively according to (5.1)

$$\omega(x) = \exp\left[-\frac{1}{k_B T}\left(S(E, V, N) - S(x|E, V, N)\right)\right] \tag{5.4}$$

Therefore we reduced the information on the thermodynamic system to the knowledge of the distribution of x. The main idea in Einstein's approach consists in the calculation of the entropy difference

δS for two states based on thermodynamic relations, i.e. the Gibbsian fundamental equation. Additionally since (5.4) is a normalized distribution we do not have to know the full thermodynamic entropy $S(E, N, V)$, but just relative changes. Further on we set $S(x|E, V, N) = S(x)$. Then obviously, is true that

$$\omega(x) = \frac{\exp[S(x)/k_B]}{\int dx \exp[S(x)/k_B]}. \tag{5.5}$$

The same result may be obtained by application of a projection technique. By introducing a δ-function we collect the microscopic probability corresponding to the value x. The conditional entropy (5.2) then reads

$$S(x|E, N, V) = k_B \ln \int d\Gamma \delta(x - x(q_1, ..., p_{3N}))\delta(H - E) \tag{5.6}$$

The probability distribution follows respectively

$$\omega(x) = \exp[-S(E, V, N)/k_B] \cdot \int d\Gamma \delta(x - x(q_1, ..., p_{3N}))\delta(H(q_1, ..., p$$

This expression is equivalent to the distribution (5.4). The present approach can also be applied to microscopic distributions under different thermodynamic constraints. For example, if x is a fluctuating value of an isothermic-isochoric system the projection pro-

cedure yields

$$\omega(x|T,V) = \exp\left[\frac{F(t,V)}{k_BT} - \frac{F(x|T,V)}{k_BT}\right] \quad (5.8)$$

where

$$F(x|T,V) == -kT\ln\int d\Gamma\delta(x - x(q_1,...,p_{3N}))\exp\left[-H(q_1,...,p_{3N}\right.$$

is the conditional free energy for the isothermic-isochoric system under the condition that x is fixed.

Let us list some general properties of the probability distribution near equilibrium. First of all looking for distributions of x around the equilibrium value x_0 the thermodynamic potentials have extremal properties with respect to x. From the second law follows $S \to max$, the maximum is reached in equilibrium, i.e. if x reaches the value x_0. Therefore an expansion around a stable equilibrium state gives

$$S(x) = S(x_0) - \frac{1}{2}k_B\beta(x - x_0)^2 \quad (5.10)$$

with

$$\beta = -\frac{1}{k_B}\left(\frac{\partial^2 S}{\partial x^2}\right) > 0. \quad (5.11)$$

This way we obtain that the fluctuations around equilibrium states are Gaussian.

$$\omega(x) = \sqrt{\frac{\beta}{2\pi}}\exp\left[-\frac{1}{2}\beta(x - x_0)^2\right] \quad (5.12)$$

The standard deviations are determined by the second derivatives of the entropy

$$\langle (x - x_0)^2 \rangle = 1/\beta \tag{5.13}$$

For other thermodynamic embeddings we obtain in an analogous way Gaussian distributions where β is the positive second derivative of the corresponding thermodynamic potential. As a concrete example we derive the distribution of the fluctuating position of a mechanical spring. It is surrounded by a gas and both the spring and the gas should be in equilibrium under the condition that the overall energy is constant. The change of the entropy of the overall system (gas and spring) can be calculated using the concept of the reversible *"Ersatzprozess"*. It yields for small deviations

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE = -\frac{1}{T} dW_{min} \tag{5.14}$$

where W_{min} is the required minimal reversible work which has to be applied to bring the spring out off equilibrium. In our case, if x_0 is the equilibrium position and χ the elasticity

$$dS = -\frac{1}{T}\chi(x - x_0)dx \tag{5.15}$$

Therefore we arrive at

$$\omega(x) = \sqrt{\frac{\chi}{2\pi k_B T}} \exp\left[-\frac{\chi(x-x_0)^2}{2k_B T}\right]. \qquad (5.16)$$

This formula played an important for the experimental determination of the Boltzmann constant k_B .

5.2 Fluctuations of many variables

In the case that there are several fluctuating variables $x_1, ..., x_s$, the variable x may be treated as a vector $\boldsymbol{x}$ with components $x_i, (i = 1...n)$ (Klimontovich, 1982, 1986). The resulting Gaussian distribution near the equilibrium state $\boldsymbol{x}_0$ reads

$$\omega(\boldsymbol{x}) = \sqrt{\frac{det\boldsymbol{\beta}}{(2\pi)^n}} \exp\left[-\frac{1}{2}\sum \beta_{ij}(x_i - x_{i0})(x_j - x_{j0})\right] \qquad (5.17)$$

with the matrix

$$\beta_{ij} = -\frac{1}{k_B}\left(\frac{\partial^2 S}{\partial x_i x_j}\right) \qquad (5.18)$$

and the second moments

$$\langle (x_i - x_{i0})(x_j - x_{j0})\rangle = (\beta^{-1})_{ij}. \qquad (5.19)$$

As an application we determine now the fluctuations of the thermodynamic variables T, V, N etc. of a subvolume which is embedded into a thermal bath with temperature T. Both bath and subvolume together

should be adiabatically isolated, i.e. their common energy, volume and particle number E, V, N are constants. Two standard problems are:
i) V is fluctuating and N is fixed, or
ii) N is fluctuating and V is fixed.
Here N, V denote the particle number and volume of the subvolume respectively. We have to calculate the entropy change of an occurring fluctuation taking into account the thermodynamic constraints. If the subvolume is a macroscopic body, this entropy change consists of two parts coming from the subvolume and from the bath, respectively

$$\Delta S_{total} = \Delta S + \Delta S_b. \tag{5.20}$$

First we let V be fluctuating and the particle number of the subvolume N be conserved. Conservation of the overall volume and energy makes the entropy change of the bath to be a function of the values for the subvolume

$$\Delta S_b = \frac{\Delta E_b + p_b \Delta V_b}{T_0} = -\frac{\Delta E + p_0 \Delta V}{T_0}. \tag{5.21}$$

Further we expand ΔE in a series for small deviations of the entropy and the volume from its equilibrium values.

$$\Delta E = T_0 \Delta S - p_0 \Delta V + \frac{1}{2}(\Delta T \Delta S - \Delta p \Delta V) \tag{5.22}$$

Combining these relations we find in quadratic approximation the probability for occurring fluctuations of the thermodynamic variables

$$W = A \exp\left[\frac{\Delta p \Delta V - \Delta T \Delta S}{2 k_B T_0}\right] \qquad (5.23)$$

Analogously we get for a fixed subvolume and a fluctuating particle number

$$W = A \exp\left[-\frac{\Delta \mu \Delta N + \Delta T \Delta S}{2 k_B T_0}\right]. \qquad (5.24)$$

We mention that in both cases the values in the exponents correspond to the negative minimal work which has to be applied to bring the subvolume to the nonequilibrium state with $\Delta T, \Delta S$ etc.. Now we remember that the deviations from equilibrium are not independent one from each other near to equilibrium. In both expressions only two variable are independent and will govern the behavior of the remaining variables by the caloric and thermic state equation. Selecting in (5.23) ΔT and ΔV as independent variables it determines the behavior of ΔS and Δp

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta p, \qquad (5.25)$$

$$\Delta p = \left(\frac{\partial p}{\partial T}\right)_V \Delta T + \left(\frac{\partial p}{\partial V}\right)_T \Delta V. \qquad (5.26)$$

This way we get the formula

$$W(\Delta T, \Delta V) = A \exp\left[-\frac{C_V}{2k_B T_0^2}(\Delta T)^2 + \frac{1}{2k_B T}\left(\frac{\partial p_0}{\partial V_0}\right)_{T_0}(\Delta V)^2\right] \quad (5.27)$$

Several interesting questions can be discussed on the basis of this expression:
First of all we see that in the linear approximation near equilibrium, extensive and intensive thermodynamic variables are decoupled. This follows from

$$\langle \Delta T \Delta V \rangle = 0 \quad (5.28)$$

and equivalently for the combination of the other variables. Further on the standard deviations of intensive variables scale with

$$\langle (\Delta T)^2 \rangle = \frac{k_B T_0^2}{C - V} \simeq \frac{1}{V_0} \quad (5.29)$$

For extensive variables the same scaling is found for the mean square deviations of relative quantities, e.g.

$$\frac{\langle (\Delta V)^2 \rangle}{V_0^2} = k_B T_0 \frac{K_T}{V_0} \quad (5.30)$$

Here K_T denotes the relative isothermic expansion coefficient

$$K_T = -\frac{1}{V_0}\left(\frac{\partial V_0}{\partial p_0}\right)_{T_0}. \quad (5.31)$$

A third point we want to discuss is the question of thermodynamic stability. Positivity of C_V and K_T is

a consequence from thermodynamic inequalities resulting from the second law. Allowing additionally fluctuation of the thermodynamic variables equilibrium is defined as the maxima of the corresponding distributions. For the particle number fluctuations we find starting from (5.24)

$$\langle(\Delta N)^2\rangle = k_B T_0 \left(\frac{\partial N_0}{\partial \mu_0}\right)_{T_0,V_0} . \tag{5.32}$$

This relation is in close relation to the stability of thermodynamic phases upon the variation of particle numbers.

5.3 Onsager's theory of linear relaxation processes

According to Einstein's view, any macroscopic quantity x may be considered as a fluctuating variable, which is determined by certain probability distribution $\omega(x)$. The mean value is given as the first moment of the probability distribution

$$x_0 =< x >= \int x \cdot \omega(x) dx. \tag{5.33}$$

In a stationary state we may shift the origin and assume $x_0 = 0$, without loss of generality. Let us assume now that the stationary state, the target of our investigation, is the state of thermodynamic equilibrium. Then $x_0 = 0$ corresponds to equilibrium and any value of $x(t)$ different from zero is strictly speak-

ing a nonequilibrium state. According to the 2nd Law, there exists a Lyapunov function and therefore the equilibrium state is an attractor of the dynamics (see section 2.2). The equilibrium state corresponds to a maximum of the entropy. This means in the present situation:

$$S(x=0) = max; \tag{5.34}$$

$$\left(\frac{\partial S}{\partial x}\right)_{x=0} = 0; \qquad \left(\frac{\partial^2 S}{\partial x^2}\right)_{x=0} \leq 0. \tag{5.35}$$

According to Onsagers's view, the relaxation dynamics of the variable x is determined by the first derivative of the entropy, which is different from zero outside equilibrium. Starting from a deviation from the equilibrium (an entropy value below the maximum) the spontaneous irreversible processes should drive the entropy to increase

$$\frac{d}{dt}S(x) = \frac{\partial S}{\partial x} \cdot \frac{dx}{dt} \geq 0. \tag{5.36}$$

In this expression two factors appear, which were interpreted by Onsager in a quite ingenious way. According to Onsager the derivative

$$X = -\frac{\partial S}{\partial x} \tag{5.37}$$

is considered as the driving force of the relaxation to equilibrium. In irreversible thermodynamics this term is called in analogy to mechanics the *thermodynamic force*, the analogy means that the (negative) entropy takes over the role of a potential. The second term

$$J = -\frac{dx}{dt} \tag{5.38}$$

is considered as the *thermodynamic flux* or *thermodynamic flow*. In a seminal paper, concerned with the question of the relaxation of nonequilibrium states to equilibrium, Onsager (1931) postulated a linear relation between the thermodynamic force and the flux

$$J = LX \tag{5.39}$$

The idea behind is, that the thermodynamics force is the cause of the thermodynamic flow and both should disappear at the same time. The coefficient L is called *Onsager's phenomenological coefficient*, or *Onsager's kinetic coefficient*. From the 2nd Law follows that the Onsager-coefficients are strictly positive.

$$P = \frac{d}{dt}S(x) = J \cdot X = L \cdot X^2 \geq 0 \tag{5.40}$$

Onsager's postulate about a linear connection between thermodynamic forces and fluxes is the origin of the development of the thermodynamics of linear dissipative system, called also *linear irreversible thermodynamics*. A remarkable property of the linear theory is the bilinearity of the entropy production

$$P = J \cdot X \tag{5.41}$$

Referring now to the fluctuation theory eq.(5.10) we find for the neighborhood of the equilibrium state the relation

$$X = -\frac{\partial S}{\partial x} = k_B \beta x \tag{5.42}$$

Using the previous equations we get finally the following linear relaxation dynamics

$$\dot{x} = -k_B L \beta x. \tag{5.43}$$

With the abbreviation

$$\lambda = L k_B \beta \tag{5.44}$$

being the so-called *relaxation coefficient* of the quantity x we get finally

$$\dot{x} = -\lambda x \tag{5.45}$$

This linear kinetic equation describes the relaxation of a thermodynamic system brought initially out of equilibrium. Starting with the initial state $x(0)$ the

dynamics of the variable $x(t)$ is

$$x(t) = x(0) \exp[-\lambda t]. \tag{5.46}$$

We see that $t_0 = \lambda^{-1}$ plays the role of the decay time of the initial deviation from equilibrium. On the other hand this coefficient which is responsible for the relaxation to equilibrium is in close relation to the fluctuation properties of the considered system. Indeed eq.(5.44) connects a kinetic property λ with a fluctuation quantity β. In this way we arrived for the first time at a so-called fluctuation-dissipation relation. In fact, Onsager assumed that deviations from equilibrium and fluctuations around the equilibrium observe the same kinetics.

Quite similar we might proceed if we are dealing with several thermodynamic values. Indeed taking the entropy in dependence on $x_i, (i = 1...N)$ the entropy production reads

$$S(x_1, ..., x_n) = S_{max} - \frac{1}{2}\beta_{ij} x_i x_j. \tag{5.47}$$

We agree, here and further on, to sum over repeating indices (Einstein's convention).

Following the Onsager ideas described above we get for the thermodynamic forces and fluxes the relations

$$X_i = -k_B \beta_{ij} x_j \tag{5.48}$$

$$J_i = -\dot{x}_i \tag{5.49}$$

The generalized linear Onsager-ansatz reads

$$J_i = L_{ij} X_j. \tag{5.50}$$

Again the 2nd law requires positivity of the entropy production. This requires

$$L_{ij} X_i X_j \geq 0 \tag{5.51}$$

for any value of X_i and disappearance only for $X_i = 0, i = 1, ..., n$. This corresponds to the requirement of positive definiteness of the matrix L_{ij}. By inserting eqs.(5.48) and (5.49) into eq.(5.50) we get

$$\dot{x}_i = -k_B L_{ij} X_j, \tag{5.52}$$

and introducing the matrix of relaxation coefficients of the linear processes near equilibrium states we end up with

$$\dot{x}_i = -\lambda_{ij} x_j, \tag{5.53}$$

$$\lambda_{ij} = k_B L_{ik} \cdot \beta_{kj}. \tag{5.54}$$

Since the matrix β_{ij} determines the dispersion of the stationary fluctuations, we have found again a close relation between fluctuations and dissipation, i.e. we have got a fluctuation-dissipation relation for a set of fluctuating and relaxing variables.

5.4 Correlations and spectra of stationary processes near equilibrium

This section is devoted to the time correlation functions and their spectrum (Klimontovich, 1982, 1986; Schimansky-Geier & Talkner, 2002). The time correlation functions will be defined here as averages over the stationary probability distribution $\omega(x)$. We consider only stationary processes and the corresponding stationary probability distributions. As a consequence of stationarity all characteristic functions depending on two times t, t' are functions of their time difference $t - t'$ only. We define the correlation function of a variable $x(t)$ as the mean over the product with the same function taken at a later time.

$$C(\tau) =< x(t)x(t+\tau) >_t = \int dx \omega(x) x(t) x(t+\tau); \qquad \tau > 0 \tag{5.55}$$

There are two equivalent ways of definition:
(i) the time average over a long (infinite) time interval,
(ii) an ensemble average based on certain probability distribution $\omega(x)$.
For the case of many fluctuating variables $x_i(t), (i = 1, ...n)$ the time correlation function is defined as

$$C_{ij}(\tau) =< x_i(t)x_j(t+\tau) >_t = \int dx_1 ... dx_n \omega(x_1, ..., x_n) x_i(t) x_j(t+\tau) \tag{5.56}$$

where $\tau > 0$ and $\omega(x_1, ..., x_n)$ stands for the simultaneous probability distribution of all x_i-variables.

We will study now several general properties of the time correlation functions.

- The first (evident) property is:
  The time correlation functions should vanish for infinitely large time and be equal to the covariance coefficient for small time

$$\lim_{t\to\infty} C_{ij}(\tau) = 0; \qquad C_{ij}(\tau = 0) = \langle x_i x_j \rangle \tag{5.57}$$

- A second property follows immediately from the stationarity: Since $C_{ij}(\tau)$ does not depend on the actual time we find by substituting $t \to t' - \tau$

$$C_{ij}(\tau) =< x_i(t)x_j(t+\tau) >=< x_i(t'-\tau)x_j(t') >= C_{ji}(-\tau) \tag{5.58}$$

We introduce now the Fourier-component of the time correlation function

$$S_{ij}(\omega) = \int_{-\infty}^{\infty} d\tau C_{ij}(\tau) \exp[i\omega\tau]. \tag{5.59}$$

This matrix function is called the spectrum of the fluctuating values. It can be calculated directly from the time correlation function via eq.(5.59). Another way is by the analysis of the dynamics of the fluctuating values. We introduce first the Fourier-components of $x_i(t)$

$$x_{i\omega} = \int_{-\infty}^{+\infty} dt x_i(t) \exp[i\omega t]. \tag{5.60}$$

We multiply this expression with $x_{j\omega}$ and average over the stationary distribution

$$< x_{i\omega} x_{j\omega'} >= \int\int_{-\infty}^{+\infty} dt dt' < x_i(t) x_j(t') > \exp[i(\omega + \omega')t + i\omega'($$

Due to the stationarity the correlator $< x_i(t) x_j(t') >$ depends on the difference $t' - t$

$$< x_{i\omega} x_{j\omega'} >= 2\pi\delta(\omega + \omega') S_{ij}(\omega). \qquad (5.62)$$

This is a form of the *Wiener-Khintchin-theorem* which connects the averaged product of the modes of a fluctuating stationary system with the spectrum of the fluctuating values. Later on we will make use of this equation.

In the last section we derived equations for the linear relaxation dynamics of macroscopic variables. Onsager stated that these equations are valid for the relaxation of fluctuations too. Indeed, in the derivation of the relaxation dynamics we never made a statement whether the initial nonequilibrium state has been prepared, as a result of an external force like usually by considering the dynamics of mean values or as the result of a spontaneous fluctuation. This way Onsager postulated the validity of these equations for the regression of fluctuating variables. As a consequence we may calculate the dynamic characteristics of fluctuations like the time correlation function from the relaxation kinetics. There exist several

approaches to prove the Onsager postulate (Klimontovich, 1982, 1986, 1995; Landau & Lifshits, 1990), we take it here as a quite evident hypothesis.
In order to calculate the correlation functions we start from the relaxation equations for the variables $x_i(t)$ which reads in the simplest case of one component $\dot{x}(t) = -\lambda x(t)$ (see previous section). We assume now that this relation is valid also for a deviation caused by a spontaneous fluctuation. We multiply the relaxation equation with the initial value $x(0)$ and find

$$\frac{d}{dt}(x(t)x(0)) = -\lambda(x(t)x(0)) \tag{5.63}$$

After averaging with respect to an ensemble of realizations we get a kinetic equation for the time correlation function

$$\frac{d}{d\tau}C(\tau) = -\lambda C(\tau) \tag{5.64}$$

with the initial conditions

$$C(\tau = 0) =< x^2 >= \int x\omega dx = \beta^{-1}. \tag{5.65}$$

By integrating (5.64) we find the explicit expression for the correlation function

$$C(\tau) = \frac{1}{\beta}\exp[-\lambda|\tau|] \tag{5.66}$$

The generalization to several fluctuating variables is straightforward. The application of Onsager's regression hypothesis leads to the kinetic equations

$$\frac{d}{d\tau}C_{ij}(\tau) = -\lambda_{ik}C_{kj} \tag{5.67}$$

with the initial condition

$$C_{ij}(0) =< x_i x_j > . \tag{5.68}$$

The most elegant method to solve these equations are one-sided Fourier-transforms (Klimontovich, 1984). We represent the time correlation functions as

$$S^{+}_{ij}(\omega) = \int_0^\infty d\tau C_{ij}(\tau)\exp[i\omega\tau] \tag{5.69}$$

The negative part of the spectrum is just the complex conjugate

$$S^{-}_{ij}(\omega) = \int_{-\infty}^0 d\tau C_{ij}(\tau)\exp[i\omega\tau] = [S^{+}_{ij}(\omega)]^* \tag{5.70}$$

Taking into account the initial conditions we find for the positive part

$$(-i\omega\delta_{ik} + \lambda_{ik})S^{+}_{kj}(\omega) =< x_i x_j > \tag{5.71}$$

From here on we consider C_{ij} and λ_{ik}, and $S^{\pm}_{ij}$ as elements of matrices $\mathbf{C}$ and Λ and $\mathbf{S}^{\pm}$. We moreover introduce the matrix $\mathbf{B} = \mathbf{C}^{-1}(0)$, and use the notation $\mathbf{I}$ for the unit matrix with elements δ_{ij}.

By adding positive and negative parts we get the complete spectrum

$$\mathbf{S}(\omega) = (-i\omega\mathbf{I} + \mathbf{\Lambda})^{-1}\mathbf{B}^{-1} + \mathbf{B}^{-1}(-i\omega\mathbf{I} + \mathbf{\Lambda})^{-1} \quad (5.72)$$

Here we have used the matrix inversion of eq.(5.71) and the symmetry relation $C_{ij}(\tau) = C_{ji}(-\tau)$, valid for stationary processes. The correlation function $C_{ij}(\tau)$ follows from the inverse Fourier transform.

In order to illustrate this procedure we take as a simple example Brownian motion, i.e. the motion of a heavy particle in a viscous liquid. As well known, this problem was first studied 100 years ago by Albert Einstein in one of his seminal papers in Annalen der Physik (**17**, 549-560 (1905)). In the next Chapters we will study Brownian motion in more detail. here we look only at its connection with the theory of linear irreversible processes. We assume for the velocity of the particle the linear equation of motion

$$\dot{v} = -\gamma_0 v. \quad (5.73)$$

For the stationary correlation function we get

$$\frac{d}{d\tau} < v(t+\tau)v(t) >= -\gamma_0 < v(t+\tau)v(t) > \quad (5.74)$$

with the initial condition

$$< v(t)^2 >= \frac{k_B T}{m}. \quad (5.75)$$

Solving these equations we find the correlation function of Brownian particles

$$< v(t+\tau)v(t) >= \frac{k_B T}{m} \exp[-\gamma|\tau|] \qquad (5.76)$$

with the spectrum

$$S_{vv}(\omega) = \frac{k_B T}{m} \frac{2\gamma_0}{\gamma_0^2 + \omega^2}. \qquad (5.77)$$

Sometimes this frequency distribution is called a red spectrum, since the maximum of intensity is at low ω. A more rich structure of the spectrum is obtained if the particle is additionally under the influence of a harmonic force. Then the dynamical equations read

$$\dot{x} = v; \qquad \dot{v} = -\gamma_0 v - \omega_0^2 x \qquad (5.78)$$

and the corresponding system of equations for the correlation functions is

$$\dot{C}_{xv}(\tau) = C_{vv}(\tau); \qquad \dot{C}_{vv} = -\gamma_0 C_{vv} - \omega_0^2 C_{xv} \qquad (5.79)$$

Following the approach described above we find the spectrum

$$S_{vv}(\omega) = \frac{k_B T}{m} \frac{2\gamma_0}{\gamma_0^2 + (\omega - \omega_0^2/\omega)^2}. \qquad (5.80)$$

This distribution has a peak at $\omega \simeq \omega_0$, a so-called resonance. Details and applications will be discussed in subsequent Chapters.

5.5 Symmetry relations and generalizations

At the end of this chapter we want to come back to the Onsager matrix of phenomenological coefficients L_{ij}, relating the thermodynamic fluxes and forces near to equilibrium. Empirically it was found that the matrix is symmetrical with respect to exchange of the indices and in a few cases one observes anti-symmetry

$$L_{ji} = \pm L_{ij}. \tag{5.81}$$

This macroscopic property means that if a force X_j will induce the thermodynamic flux J_i we will find also a flux J_j generated by the force X_i. This circumstance, was also found already in Onsager's paper.
For the proof of this relation we use properties of the correlation function, in particular $C_{ij}(\tau) = C_{ji}(-\tau)$. The second fact which has to be taken into account is that the fluctuating values are functions of the microscopic variables. Therefore it holds

$$x_i(t) = \epsilon_i x_j(-t) \tag{5.82}$$

which expresses the reversibility of the microscopic motion. Here ϵ is the parity coefficient which is $+1$ for even variables and -1 for odd ones. It yields that

$$C_{ij}(\tau) =< x_i(t)x_j(t+\tau) >= \epsilon_i\epsilon_j < x_i(-t)x_j(-t-\tau) >= \epsilon_i\epsilon_j C_{ij}(-$$

Taking into account the stationarity condition we find

$$C_{ij}(\tau) = \epsilon_i \epsilon_j C_{ji}(\tau). \tag{5.84}$$

As a consequence of the general regression dynamics we find the following dynamical equations for the correlation functions

$$\frac{d}{d\tau} C_{ij}(\tau) = -\lambda_{ik} C_{kj}(\tau). \tag{5.85}$$

Hence we obtain

$$\lambda_{ik} C_{kj}(\tau) = \epsilon_i \epsilon_j \lambda_{jk} C_{ki}(\tau). \tag{5.86}$$

For $\tau = 0$ the correlation function reduces to the standard deviation with $C_{ij}(0) = [\beta_{ij}]^{-1}$; using further the definition of the relaxation coefficients λ_{ij} we get finally the famous *Onsager-Casimir symmetry relation*

$$L_{ji} = \epsilon_i \epsilon_j L_{ij}. \tag{5.87}$$

This relation is one of the fundamentals of linear irreversible thermodynamics; it is well confirmed by many experiments.

The approach presented so far in this Chapter is restricted to irreversible processes close to equilibrium. The extension to far from equilibrium situations is extremely difficult. There exist many approaches to

solve this problem. We mention the early work of Onsager and Machlup (1953), of Machlup and Onsager (1953), of Ginzburg and Landau (1965), and of Glansdorff and Prigogine (1971). An advanced theory of nonlinear irreversible processes is due to the work of the late Rouslan Stratonovich (Stratonovich, 1994). We mention also the extended thermodynamics and other new approaches (Muschik, 1988; Jou, Casas-Vazques & Lebon, 1993; Ebeling & Muschik, 1993; Luzzi, Vasconcellos & Ramos, 2000). Special attention deserves a new approach (Grmela & Öttinger, 1997), named GENERIC (general equations for the nonequilibrium reversible-irreversible coupling), which seems to contain most of the theories mentioned above as special cases (Öttinger, 2005). We will give here only one of the basic ideas. The general time-evolution equation postulated by Grmela and Öttinger is of the following structure:

$$\frac{dx}{dt} = L\frac{\delta E}{\delta x} + M\frac{\delta S}{\delta x}. \tag{5.88}$$

Here x represents a set of independent variables, in many cases x will depend on continuous position-dependent fields, such as mass, momentum, and energy densities. Further, E and S are the total energy and entropy expressed in terms of the state variables, and L and M are certain linear operators or matri-

ces. The application of a linear operator may include integrations over continuous labels and then $\delta/\delta x$ typically implies functional rather than partial derivatives.

There is no room here to go into the details of these more or less fruitful but not exhaustive methods. The whole field is still in development.

Chapter 6

Nonequilibrium Distribution Functions

6.1 A simple example – driven Brownian particles

The general theory of nonequilibrium systems is still in the first stages of development. At present we have a well developed theory of ideal gases going back to *Boltzmann*. We presented the main ideas of this rather old theory already in the 3rd Chapter. Further we have a nice theory for small (linear) deviations from equilibrium, which essentially goes back to Einstein and Onsager, this theory was presented in Chapter 5. A theory of the same generality as the Gibbs theory of equilibrium systems does not exist yet. In particular the formulation of the statistical mechanics of far-from equilibrium systems is an extremely difficult task which is full of surprises and interesting applications to many interdisciplinary fields (Haken, 1973, 1983; Klimontovich, 1995: Zubarev, 1976: Schimansky-Geier & Pöschel, 1997). On the other hand we may treat many spe-

cial examples, several of them will presented in this and in the following sections. We will start again with a treatment of Brownian motion and related phenomena and will finish this Chapter with general information-theoretical methods.

In order to bring a system to nonequilibrium we need some driving force. Historically the first case of a treatment of driven systems is connected with the theory of sound developed in the 19th century by Helmholtz and Rayleigh. The treatment of these early models will lead us later to other interesting applications as the theory of driven Brownian particles. This is a unification of the model of Brownian motion due to Einstein, Smoluchowski and Langevin with the model of (acoustic) oscillators driven by negative friction developed by Rayleigh, Helmholtz, van der Pol and many other workers. We will use here the definitions and results introduced in Sections 2.4 and 2.5.

Let us study at the beginning a force-free Brownian particles on a line ($d = 1$) under equilibrium conditions. Using the phenomenological method we find the Maxwellian distribution, which is a special case of the canonical distribution function defined in

sections 4.3-4.4:

$$f_0(\mathbf{v}) = \rho(H) = C \exp\left[-\frac{mv^2}{2k_B T}\right]. \tag{6.1}$$

There is an alternative method to derive this distribution based on the Langevin-Fokker-Planck method. We start from the Langevin equation (see section 2.5)

$$\frac{dv}{dt} = -\gamma_0 v + (2D_v)^{1/2}\xi(t) \tag{6.2}$$

which describes standard Brownian motion in equilibrium systems (γ_0 - friction coefficient, D_v- diffusion constant for the velocities). The corresponding Fokker-Planck equation reads (see section 2.5)

$$\frac{\partial P(v,t)}{\partial t} = \frac{\partial}{\partial v}\left[\gamma_0 v P(v,t) + D_v \frac{\partial P(v,t)}{\partial v}\right] \tag{6.3}$$

This equation is solved by the Gaussian distribution

$$f_0(v) = C \exp\left[-\frac{\gamma_0 v^2}{2D_v}\right]. \tag{6.4}$$

The Gaussian corresponds to the equilibrium Maxwell distribution just in the case that the so-called *Einstein relation*

$$D_v = \frac{k_B T \gamma_0}{m} \tag{6.5}$$

holds. This case will be studied in more detail in Chapters 6-9. Here we are more interested in the

transition to non-equilibrium situations when eqs.(6.4) and (6.5) are not observed. In this case the system might be driven away from equilibrium; then we speak about active Brownian motion. The corresponding Langevin equation of motion reads ($m = 1$):

$$\frac{dv}{dt} = F(v) + (2D(v))^{1/2}\xi(t) \qquad (6.6)$$

Here $F(v)$ is the dissipative force acting on the particle and $D(v)$ a diffusion function. The simplest case

$$F(v) = -\gamma_0 v; \qquad D(v) = D_v = const \qquad (6.7)$$

leads as back to standard Brownian motion. Now we will consider nonequilibrium situations corresponding to nonlinear expressions for the force. Models of nonlinear dissipative forces were first considered for a one-dimensional oscillation problem by Rayleigh (1894) who studied in his *"Theory of Sound"* the case

$$F(v) = (a - bv^2)v; \qquad D(v) = 0 \qquad (6.8)$$

with $b > 0$. Then the equation of motion has for $a < 0$ the only stationary state $v = 0$ and for $a > 0$ it possesses two stationary states

$$v = \pm v_0; \qquad v_0 = \sqrt{\frac{a}{b}} \qquad (6.9)$$

The point $a = 0$ corresponds to a kinetic phase transition which possesses quite interesting properties (Klimontovich, 1982, 1986; Haken, 1983; Horsthemke & Levefer, 1984). Klimontovich (1982,1986) studied this system in much detail including a Langevin source with constant noise. Assuming $m = 1$ the Hamiltonian is $H = v^2/2$. We see that the dissipative force is fully determined by the Hamiltonian

$$F(v) = -(a - 2bH)v \tag{6.10}$$

Such systems are called "canonical dissipative". This rather interesting class of systems will be analyzed in more detail in the next section. The Fokker-Planck equation reads now

$$\frac{\partial P(v,t)}{\partial t} = \frac{\partial}{\partial v}\left[(2bH - a)vP(v,t) + D_v \frac{\partial P(v,t)}{\partial v}\right] \tag{6.11}$$

This equation has the following solution which represents a stationary distribution function (Klimontovich, 1982, 1986)

$$f_0(v) = \rho(H) = C \exp\left[-\frac{aH - bH^2}{D_v}\right]. \tag{6.12}$$

For $a < 0$ this distribution is quite similar to a Maxwellian. For $a > 0$ the system is driven away from equilibrium. In this case the velocity distribution is bistable and has two maxima in the velocity

space. The maximum of the energy distribution corresponds to

$$H_0 = \frac{v_0^2}{2} = \frac{a}{2b}; \qquad v_0^2 = \frac{a}{b}$$

This corresponds to a system of particles which move all either with velocity v_0 to the right or with $-v_0$ to the left. The picture is like a hydrodynamic flow to the right or to the left. Lateron we will discuss interesting biological applications to the movement of swarms (see Chapter 12).

The theory given above may be easily generalized to self-oscillating systems of a special type, discussed briefly already in Section 2.4, which have the equation of motion (Klimontovich, 1982, 1986)

$$\frac{dv}{dt} + \omega_0^2 x = (a - bH)v + (2D_v)^{1/2}\xi(t) \qquad (6.13)$$

Here the Hamiltonian is given by ($m = 1$):

$$H = \frac{1}{2}v^2 + \frac{1}{2}\omega_0^2 x^2. \qquad (6.14)$$

Again the friction force is determined by a Hamiltonian, corresponding to the so-called canonical-dissipative structure. Let us first discuss the stationary state for $D = 0$. An exact solution of the dynamic equations

is

$$x(t) = (v_0/\omega_0)\sin(\omega_0 t+\delta); \qquad v(t) = v_0\cos(\omega_0 t+\delta) \tag{6.15}$$

The stationarity requires

$$H = H_0 = v_0^2 = a/b. \tag{6.16}$$

This is a sustained oscillation with stationary amplitude $x_0 = v_0/\omega_0$. Due to the canonical-dissipative character we may find again an exact solution for the stationary Fokker-Planck equation, which is similar to eq. (6.12). We find

$$f_0(v) = \rho(H) = C\exp\left[-\frac{aH - bH^2/2}{D_v}\right]. \tag{6.17}$$

Here we have to observe the different expression for the Hamiltonian H and consequently also for the normalization C. For the passive case $a < 0$ we may neglect the nonlinearity putting $b = 0$ and find simply a Maxwellian.

$$f_0(v) = \rho(H) = C\exp\left[-\frac{-|a|H}{D_v}\right] \tag{6.18}$$

For $a = 0$ we observe in the deterministic system a bifurcation which leads to the auto-oscillating regime. The distribution function for the transition point reads:

$$f_0(v) = \rho(H) = C\exp\left[-\frac{bH^2}{D_v}\right] \tag{6.19}$$

We notice the large dispersion which is characteristic for all phase transitions. The first moments of this distribution are (Klimontovich, 1982, 1986)

$$< H >= \frac{2}{\sqrt{\pi}}\sqrt{\frac{D_v}{2b}}; \qquad < H^2 >= \frac{D_v}{b} \tag{6.20}$$

In the case of driven motion $a > 0$, that means for the regime of developed oscillations, the distribution reads

$$f_0(v) = \rho(H) = C \exp\left[-\frac{b(H - a/b)^2}{2D_v}\right] \tag{6.21}$$

where the constant follows again from normalization (Klimontovich, 1982, 1986).

$$C = \sqrt{\frac{2b}{\pi D}}\left[1 + \Phi\left(\frac{a}{\sqrt{2bD_v}}\right)\right]^{-1}.$$

Here $\Phi(x)$ is the standard error function. We can easily check that the curve of maximal probability has the shape of a crater. In the limit of small noise ($D_v \to 0$) the curve of maximal probability is exactly above the deterministic limit cycle. This is, of course, a necessary condition which any correct solution of the Fokker-Planck equation has to fulfill. Further we note, that the exponent $(H - a/b)^2$ correspond to the Lyapunov function of the system identified in Section 2.4. We found this way a model sys-

tem which is exactly solvable in equilibrium and for any distance from equilibrium. Admittedly the force function which we used $F = (a - bH)v$ is not very realistic from the physical point of view, however it may be shown, that the more realistic Rayleigh force $F = (a - bv^2)v$ introduced for modeling sound oscillations as well as the van der Pol force $F = (a - bx^2)$ introduced for modeling electric oscillations may be converted in good approximation to our canonical-dissipative force $F = (a - bH)v$. This may be shown by using the procedure of phase-averaging (Klimontovich, 1982, 1986). We may use our model system as a good testing ground for more advanced methods of nonequilibrium theory. A special conclusion is, that the stationary distribution functions may depend not only on invariants as in our case H, but also on higher powers of the invariants, as in our case H^2.

6.2 Canonical-dissipative systems

As we have seen in the previous section, there exist systems, were the dissipative forces are determined by the Hamiltonian, which allows for exact solutions. Now we will generalize this concept and treat a whole class of solvable systems. This idea is mainly based on works of *Haken and Graham*

(Haken, 1973, Graham, 1981). We will show that at least for this special class of far from equilibrium systems, the so-called canonical-dissipative systems, a general ensemble theory similar to Gibbs approach may be developed (Graham, 1981; Ebeling, 1981, 2000, 2002; Feistel and Ebeling, 1989). The theory of canonical-dissipative systems is the result of an extension of the statistical physics of Hamiltonian systems to a special type of dissipative systems where conservative and dissipative elements of the dynamics are both determined only by invariants of the mechanical motion. This theory is in close relation to the simple example of driven Brownian motion and auto-oscillating systems, presented in the first section of this Chapter. Later we will show a close relation to a recently developed theory of active Brownian particles (Schweitzer et al., 1998; Ebeling et al., 1999; Erdmann et al., 2000; Schweitzer et al., 2001; Schweitzer, 2003). The main ideas of the theory of active Brownian motion will be explained in Chapter 12.

We start the development of the theory of canonical-dissipative systems with a rather general study of the phase space dynamics of a driven many-particle system with f degrees of freedom $i = 1, ..., f$. Assuming that the Hamiltonian is given by $H(q_1...q_f p_1...p_f)$ the mechanical motion is given by Hamilton equa-

tions. The solutions are trajectories on the plane $H = E = const$. The constant energy $E = H(t = 0)$ is given by the initial conditions, which are (in certain limits) arbitrary. We construct now a canonical-dissipative system with the same Hamiltonian (Haken 1973; Graham 1981; Ebeling, 2000; Schweitzer et al., 2001)

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} - g(H)\frac{\partial H}{\partial p_i} \tag{6.22}$$

We will assume that the dissipation function $g(H)$ is nondecreasing. Equation (6.22) defines a canonical-dissipative system which does not conserve the energy. In regions of the phase space where $g(H)$ is positive, the energy decays and in regions where $g(H)$ is negative, the energy increases. The simplest possibility is constant friction $g(H) = \gamma_0 > 0$ which corresponds to a decay of the energy to the ground state. Of more interest is the case when the dissipative function has a root $g(E_0) = 0$ at a given energy E_0. Then the states with $H < E_0$ are supported with energy, and from states with $H > E_0$ energy is extracted. Therefore any given initial state with $H(0) < E_0$ will increase its energy up to reaching the shell $H(t) = E_0$ and any given initial state with $H(0) > E_0$ will decrease its energy up to the moment when the shell $H(t) = E_0$ is reached. Therefore

$H = E_0$ is an attractor of the dynamics, any solution of eq.(6.22) converges to the surface $H = E_0$. On the surface $H = E_0$ itself the solution corresponds to a solution of the original Hamiltonian equations for $H = E_0$. The simplest dissipation function with the wanted properties is a linear function

$$g(H) = c(H - E_0) \tag{6.23}$$

The speed of the relaxation process is proportional to c^{-1}. The linear dissipative function (6.23) has found applications to Toda chains (Makarov et al., 1999). More general dissipative functions were considered in the theory of active Brownian motions (Schweitzer et al., 1998; Ebeling et al., 1999; Erdmann et al., 2000). We mention that all noninteracting systems $H = H(\boldsymbol{p}^2)$ with $g = g(\boldsymbol{p}^2)$ are canonical-dissipative. The attractor of the dissipative system (6.22) is located on the surface $H = E_0$. This does not mean that the full $(2f - 1)$-dimensional surface is the attractor of the system. Such a statement is correct only for the case $f = 1$, which has been considered in the last section, further this statement may be true also for systems which are ergodic on the surface $H = E_0$. In the general case the attractor may be any subset of lower dimension, possibly even a fractal structure. Let us consider for example the case of one particle

moving in an external field with radial symmetry

$$H = \frac{\mathbf{p^2}}{2m} + U(r); \qquad \boldsymbol{p} = m\boldsymbol{v}. \tag{6.24}$$

Then the equation of motion reads

$$\frac{d\mathbf{p}}{dt} = -\frac{\partial H}{\partial \mathbf{r}} - g(H)\mathbf{v}. \tag{6.25}$$

The corresponding equation for the angular momentum $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ reads

$$\frac{d\boldsymbol{L}}{dt} = -\frac{1}{m} g(H)\boldsymbol{L}. \tag{6.26}$$

We see that on surfaces with $g(H) = 0$ obligatory $\mathbf{L} = \mathbf{L_0} = const$ holds. Of special interest are cases where this constant is different from zero. In other words, the system shows rotations. The concrete value of $\mathbf{L_0}$ may be obtained by explicit solutions of the equations of motion on the surface $H = E_0$.
A more general class of canonical-dissipative systems is obtained, if beside the Hamiltonian also other invariants of motion are introduced into the driving functions. Let us assume that the driving functions depend on $H = I_0$ and also on some other invariants of motion $I_0, I_1, I_2, ..., I_s$ for example

- $\mathbf{I}_1 = \mathbf{P}$ - total momentum of the system,
- $\mathbf{I}_2 = \mathbf{L}$ - total angular momentum of the system.

  etc.

For the equation of motion we postulate

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} - \frac{\partial G(I_0, I_1, I_2, ...)}{\partial p_i}. \tag{6.27}$$

We include now an external white noise source restricting now our study to the case were the dynamics is determined by H. The Langevin equations read

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} - g(H)\frac{\partial H}{\partial p_i} + (2D(H))^{1/2}\xi(t) \tag{6.28}$$

The essential assumption is, that noise and dissipation depend only on H. The corresponding Fokker-Planck equation reads

$$\frac{\partial \rho}{\partial t} + \sum \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \sum \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} \tag{6.29}$$

$$= \sum \frac{\partial}{\partial p_i}\left[g(H)\frac{\partial H}{\partial p_i}\rho + D(H)\frac{\partial \rho}{\partial p_i}\right] \tag{6.30}$$

An exact stationary solution is

$$\rho_0(q_1...q_f p_1...p_f) = Q^{-1}\exp\left(-\int_0^H dH' \frac{g(H')}{D(H')}\right) \tag{6.31}$$

The derivative of ρ_0 vanishes if $g(H = E_0) = 0$. This means the probability is maximal at the surface $H = E_0$.

For the special case of a linear dissipation function

we find a stationary solution

$$\rho_0(q_1...q_f p_1...p_f) = Q^{-1} \exp\left(\frac{cH(2E_0 - H)}{2D}\right) = Q_1^{-1} \exp\left(\frac{-c(H -$$
(6.32)

The problem with these distributions is, that they might be formally exact but nevertheless lacking physical meaning. In particular, distributions of type (6.31) do not admit translational or rotational flows, since

$$\langle p_i \rangle = 0; \qquad \langle L_i \rangle = 0 \tag{6.33}$$

holds for symmetry reasons. Let us consider for example a mass point rotating in a central field on a plane. Then $H = E_0$ is a sphere in a 4-dimensional space. Since the angular momentum has only two possible directions (up or down), corresponding to right or left rotations, the system is unable to fill the whole surface $H = E_0$ but just a part of it, compatible with these two possibilities of left or right rotations. The easiest way to admit rotations is to include, as for the equilibrium case explained in Section 4.4., the invariant $\boldsymbol{\Omega} \cdot \boldsymbol{L}$ into the distribution

$$\rho_0(q_1...q_f p_1...p_f) = Z^{-1}(\Omega') \exp\left(-\int_0^H dH' \frac{g(H')}{D(H')} + \boldsymbol{\Omega}' \cdot \boldsymbol{L}\right)$$
(6.34)

This distribution admits rotations due to the different symmetry character. The mean value of the angular momentum is given by

$$\langle \boldsymbol{L} \rangle = \frac{\partial \ln Z(\boldsymbol{\Omega}')}{\partial \boldsymbol{\Omega}'}. \tag{6.35}$$

By replacing the mean value by the deterministic value $\boldsymbol{L}_0$

$$\boldsymbol{L}_0 = \frac{\partial \ln Z(\boldsymbol{\Omega}')}{\partial \boldsymbol{\Omega}'} \tag{6.36}$$

we may get a good approximate solution, reflecting the most important physical properties of our dynamical system. More general forms of the distribution will be discussed in Section 5.5. The existence of exact solutions for the probability distributions admits to derive the thermodynamic functions as the mean energy and the entropy. The system has further a Lyapunov functional K which is provided by the Kullback entropy which is a nonincreasing function

$$K[\rho, \rho_0] = \int dq_1 ... dq_f dp_1 ... dp_f \rho \log[\rho/\rho_0]. \tag{6.37}$$

This theorem governs the approach to the stationary state.

6.3 Microcanonical non-equilibrium ensembles

As shown above, canonical-dissipative forces drive the system to certain subspaces of the energy surface, where the total momentum or the angular momentum are fixed. In many cases the system is ergodic on these surfaces; this question has to be checked separately for any special case. Assuming that ergodicity (quasi-ergodicity) is given we may postulate that in the long run the measure of the trajectories is equally distributed on certain shells around the surfaces

$$H(q_1...q_f p_1...p_f) = E_0, \tag{6.38}$$

$$I_k(q_1...q_f p_1...p_f) = I_k, k = 2, 3, ..s. \tag{6.39}$$

The idea about the ergodicity of the trajectories leads us to microcanonical ensembles. There exist many examples of physical systems which are well described by microcanonical ensembles (Gross, 2001). Here we consider systems which are uniform in space but far from equilibrium. As examples may serve laser plasmas, homogeneous turbulent fluids and systems of active Brownian particles. These systems have in common, that they are driven by energy supply to far from equilibrium states. We construct now a special non-equilibrium ensemble which is characterized

by a constant probability density on a energy shell

$$E_0 - \frac{1}{2}\delta E \leq H(q_1...q_f p_1...p_f) \leq E_0 + \frac{1}{2}\delta E. \quad (6.40)$$

This is a rather restrictive assumption, in particular it means that due to the symmetry of the system all mean fluxes are zero. The mean energy of the ensemble is fixed $\langle H \rangle = E_0 = U.$ and the entropy is given by the volume of the energy shell according to Boltzmann's formula. Since our system is not in thermal equilibrium, not all thermodynamic relations, e.g.the relation between energy and temperature, are valid. The most typical properties of an equilibrium ensemble is, that the mean energy is proportional to the noise level T and that the mean quadratic deviation $\langle (\delta H)^2 \rangle$ is proportional to T^2. In the equilibrium all energy comes from the thermal fluctuations. In nonequilibrium the energy of the nonlinear excitations and the noise energy are decoupled. In other words, the energy $\langle H \rangle = U \simeq E_0$ is given mostly by the properties of the energy source and is nearly independent of the noise level which we will denote from now by D. On the other hand the energy fluctuations depend strongly on the noise strength D and are nearly independent on the energy of the excita-

tions

$$\left(\delta E^2\right) = \left(\langle H^2\rangle - \langle H\rangle^2\right) \simeq D. \qquad (6.41)$$

We see immediately that the canonical distribution is not compatible with these properties. By constructing other exponential distribution functions from the maximum entropy principle we have to observe the correct behavior of the mean and the dispersion (Ebeling & Röpke, 2004). The most simple example of a distribution with the right properties is the Gaussian eq.(6.32). As an example may serve a nonequilibrium gas where all particles move with the same modulus of the velocity $\boldsymbol{v}_i = v_0^2$, a so-called isokinetic ensemble (Hoover, 2001). The direction of the velocities fluctuates stochastically. A physical system which behaves in such a way is a fluid in the state of uniform turbulence. Other examples are strongly excited laser plasmas and active Brownian particles.

In a generalization of the approach described above we assume that beside the energy also some other invariants of motion as e.g. the momentum or the angular momentum are conserved. Then the generalized microcanonical ensemble assumes that the probability density is constant on the shells around

the prescribed invariants

$$I_k - \frac{1}{2}\delta I_k \leq I_k(q_1...q_f p_1...p_f) \leq I_k + \frac{1}{2}\delta I_k \quad (6.42)$$

for $k = 0, 1, ..., s$. This means that the density is concentrated on certain submanifolds of the energy shell $k = 0$. We note that the invariants are not necessarily smooth functions. Fluxes may be prescribed as far as they are expressed by invariants of motion, e.g a macroscopic flow may be prescribed by the total momentum $\boldsymbol{I}_1 = \boldsymbol{P}$. The entropy is given by the Boltzmann formula

$$S = k_B \log \Omega(I_0, I_1, ..., I_s). \quad (6.43)$$

where Ω expresses the volume of the manifold defined by the fixed invariants of motion.

6.4 Systems driven by energy depots

We started this Chapter with an example of a driven system far from equilibrium which goes back to to Klimontovich (1982, 1986, 1995). The simple Klimontovich system, which allows a full treatment, is a unification of the model of Brownian motion due to Einstein, Smoluchowski and Langevin with the model of (acoustic) oscillators driven by negative friction which originally is due to Rayleigh and Helmholtz. A "minus" of this nice model is it purely phenomenolog-

ical character. We did not touch at all the question, where the forces, driving the system out of equilibrium, may come from. Let us start from a Langevin equation for a particle with coordinate $\boldsymbol{r}$ and velocity $\boldsymbol{v}$:

$$m\frac{d\boldsymbol{v}}{dt} + \nabla U(\boldsymbol{r}) = \boldsymbol{F}(\boldsymbol{v}) + m(2D_v)^{1/2}\boldsymbol{\xi}(t). \quad (6.44)$$

Now we will derive the dissipative force $\boldsymbol{F}(\boldsymbol{v})$ in a more physical way from energy depot models. There are many possibilities to couple a system to energy reservoirs. We will start with the treatment of two different variants. The first variant of the depot model (SET-model) developed in (Schweitzer et al., 1998, Ebeling et al., 1999) is based on the ansatz

$$\boldsymbol{F}(\boldsymbol{v}) = m\boldsymbol{v}(de - \gamma_0) \quad (6.45)$$

where e is the energy content of a depot and d a conversion parameter. The first term expresses an acceleration in the direction of $\boldsymbol{v}$. The second term $m\gamma_0\boldsymbol{v}$ is the usual passive friction, which by assumption is connected with the noise by an Einstein relation $D_v = \gamma_0 k_B T/m$. We assume further that the Brownian particles are able to take up energy with the rate q, which can be stored in the depot e. This internal energy can be converted into kinetic energy with a momentum dependent rate $d\boldsymbol{v}^2$, which results

in the acceleration in the direction of movement. The internal energy dissipates with the rate ce, The balance of the depot energy then reads

$$\frac{de}{dt} = q - ce - de\boldsymbol{v}^2. \tag{6.46}$$

The energy balance of the particle follows by multiplying the Langevin equation with the velocity v, we get

$$\frac{dH}{dt} = dem\boldsymbol{v}^2 - m\gamma_0\boldsymbol{v}^2 + m\boldsymbol{v}\sqrt{2D_v}\cdot\boldsymbol{\xi}(t). \tag{6.47}$$

Assuming $q > 0$ and requiring that the internal energy depot relaxes fast compared to the motion of the particle we get in adiabatic approximation for the *depot model*

$$\boldsymbol{F} = m\boldsymbol{v}\left(\frac{dq}{c + dv^2} - \gamma_0\right) \tag{6.48}$$

For sufficiently large values of q and d the friction function may have a zero at

$$\boldsymbol{v}_0^2 = \frac{q}{\gamma_0} - \frac{c}{d} = \frac{c}{d}\zeta \tag{6.49}$$

$$\zeta = \frac{qd}{c\gamma_0} - 1$$

For positive values of the bifurcation parameters ζ and small velocities $|\boldsymbol{v}| < v_0$, we observe input of free

energy, the system is driven (self-propelling). Another convenient way of writing the friction function is

$$\gamma(v^2) = \gamma_0(1 - \frac{\delta}{1 + v^2/v_1^2}) \qquad (6.50)$$

with $v_1^2 = c/d$ and $\delta = \zeta + 1$. This friction force was first studied in (Schweitzer et al., 1998; Ebeling et al., 1999; Erdmann et al., 2000). The parameter $v_1 > 0$ is connected to internal dissipation and δ controls the conversion of the energy taken up from the external field into kinetic energy. Actually, the parameter δ is now the essential bifurcation parameter of this model. The parameter value $\delta = 0$ corresponds to equilibrium, the region $0 < \delta < 1$ stands for nonlinear passive friction and $\delta > 1$ corresponds to active friction. The value of the transition (bifurcation) from one to the other regime is $\delta = 1$. For the passive regime $0 < \delta < 1$ the friction function has one zero point at $v = 0$ which is the only attractor of the deterministic motion. In Fig. (6.1) we represented the velocity-dependent friction for different values of driving. Without noise all particles come to rest at $v = 0$. For $\zeta > 1$ the point $v = 0$ becomes unstable but we have now two additional zeros at

$$v = v_0 = \pm v_1\sqrt{\delta - 1} \qquad (6.51)$$

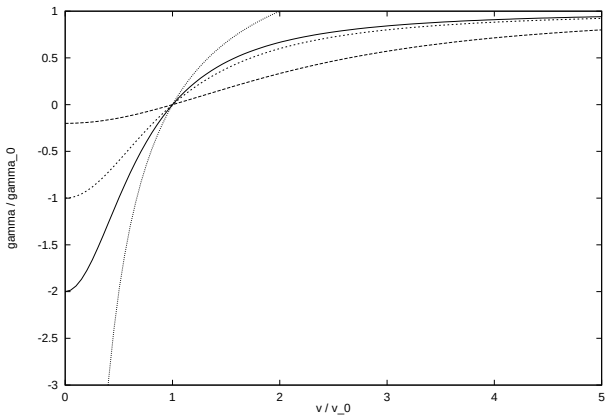

Fig. 6.1 Friction function for several values of the driving strength.

These two velocities are the new attractors of the free deterministic motion if $\delta > 1$. In Fig. 6.2 we have plotted the friction force for the two values $\delta = 0$ (equilibrium) and $\delta = 2$ (strong driving). The fig-

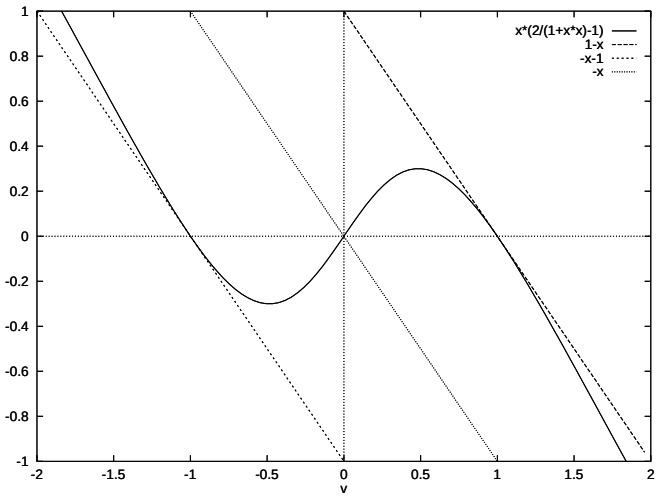

Fig. 6.2 Dissipative force for the parameter values $\delta = 0$ (equilibrium) and $\delta = 2$ (strong driving) and a piecewise linear approximation for $\delta = 2$.

ure includes the representation of a useful piecewise linear approximation of the friction force for $\delta > 1$

which reads

$$\boldsymbol{F} = -m\gamma_1 \boldsymbol{v}\left[1 - \frac{v_0}{|v|}\right], \qquad (6.52)$$

$$\gamma_1 = 2\gamma_0 \frac{\delta - 1}{\delta}$$

This is a linear approximation to the friction force near to the two stable velocities $v = \pm v_0$. We see also that between the zero points the force function may be well approximated by a cubic law

$$\boldsymbol{F} = m\boldsymbol{v}\left[a - bv^2\right] \qquad (6.53)$$

with $v_0^2 = a/b$. This simple law was introduced already in the 19th century by Lord Rayleigh in his *"Theory of sound"* (Rayleigh, 1893). One-dimensional stochastic systems with a friction function corresponding to Rayleigh's law were discussed in detail by Klimontovich (1983, 1995).

The piecewise linear friction function introduced above as an approximation is similar to the friction law found empirically by Schienbein and Gruler from experiments with cells (Schienbein & Gruler, 1993; Schienbein et al., 1994). The Schienbein-Gruler function reads

$$\mathrm{F} = -m\gamma_0 \boldsymbol{v}\left[1 - \frac{v_0}{|v|}\right]. \qquad (6.54)$$

The asymptotics of the depot model (SET-model) is in agreement with the Schienbein-Gruler model; in both cases we have the asymptotics $-\gamma_0 \boldsymbol{v}$. In the zero point v_0 the derivative in the zero point is in the SET-model $-\gamma_1$ and in the Schienbein Gruler law it is fixed by γ_0.

Let us come now to the question of the distribution functions. The systems of active Brownian particles introduced above are canonical dissipative systems in the sense discussed in the previous section. Therefore the distribution function can be given exactly. On order to prove this we write

$$\boldsymbol{F} = -m\boldsymbol{v}\gamma(v^2) \tag{6.55}$$

Since v^2 is proportional to the kinetic energy - and there is no potential energy so far - this system is indeed canonical-dissipative. Based on the canonical-dissipative character we find in the general case the distribution function

$$\rho = C \exp\left(-\frac{m}{2D_v}\int \gamma(v^2)dv^2\right). \tag{6.56}$$

Let us discuss now more concrete cases. The distribution for the depot model (SET- model) reads:

$$\rho_0(v_x, v_y) = C \exp\left[-\frac{mv^2}{2kT} + \frac{q}{2D_v}\log\left(1 + \frac{d}{c}v^2\right)\right] \tag{6.57}$$

Approximately this may be written as

$$\rho_0(v_x, v_y) = C \exp\left[-\frac{qd^2}{4D_v c^2}(v^2 - v_0^2)^2\right]. \quad (6.58)$$

For piecewise linear force laws, including the Schienbein-Gruler law, the distribution is of particular simplicity

$$\rho(v_x, v_y) = C \exp\left(-\frac{\gamma_1}{2D_v}(|\boldsymbol{v}| - v_0)^2\right) \qquad (6.59)$$

The piecewise linear force law may be used as an ap-

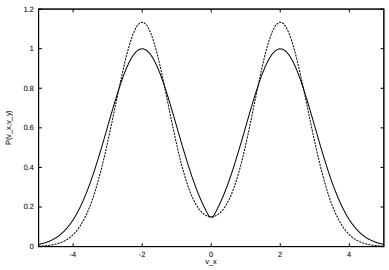

Fig. 6.3

Distribution function of the velocity for the depot model (dashed line) and for the piecewise linear approximation (full line). (Parameters: $D_v = \gamma_0 = c = d = 1, q = 5, v_0 = 2$*.)*

proximation for arbitrary friction laws of type (6.55). Since the modulus of $\boldsymbol{v}^2$ is most time around the value v_0^2 the linearization is well justified. Due to the simplicity of piecewise linear friction laws we are able to find also several more general solutions. In particular the *mean square displacement* may be calculated (Schienbein et al., 1994; Mikhailov & Meinköhn, 1997;

Erdmann et al., 2000)

$$\left\langle (\boldsymbol{r}(t) - \boldsymbol{r}(0))^2 \right\rangle = \frac{2v_0^4}{D_v} t + \frac{v_0^6}{D_v^2} \left[\exp\left(-\frac{2D_v t}{v_0^2} \right) - 1 \right]. \tag{6.60}$$

The analytical expressions for the stationary velocity distribution and for the mean squared displacement are in good agreement with computer simulations (Schweitzer et al., 2001) and with measurements on the active movements of granulocytes (Schienbein & Gruler, 1993; Schienbein et al., 1994). We notice also the close relation of this theory to systems with isokinetic thermostats (Hoover et al., 1987; Hoover, 2001). Driving by velocity-dependent dissipative forces may have similar effects as driving by isokinetic thermostats as will be shown in the next section. In the adiabatic approximation all the models discussed above have similar properties, in particular they are of canonical-dissipative form.

Summarizing the results of this and the previous sections we underline that these studies were limited to a rather special type of nonequilibrium systems which are pumped from external sources with free energy. We started from the Hamiltonian theory of mechanical systems and constructed forces to drive them away from equilibrium. Then in order to extend the

known methods of statistical physics for conservative systems to dissipative systems we developed a general theory of canonical-dissipative systems. Special canonical-dissipative system were constructed, which solution converges to the solution of the conservative system with given energy, or other prescribed invariants of motion. In this way we were able to generate nonequilibrium states characterized by certain prescribed invariants of mechanical motion. We postulated special distributions which are analogues of the microcanonical ensemble in equilibrium. Further we found solutions of the Fokker-Planck equation which may be considered as analogues of the canonical equilibrium ensembles. We proposed to call these distributions canonical-dissipative ensembles. By the help of the explicit nonequilibrium solutions we were able to construct for canonical-dissipative systems a complete statistical thermodynamics including an evolution criterion for the nonequilibrium.

In Chapter 12 we will study applications of the theory to problems of active Brownian motion. We will show that this class on systems is of interest for modeling biological motion (Gruler & Schienbein, 1993, Schweitzer, 2002) and traffic (Helbing, 1997, 2001). Finally we want to say, that canonical-dissipative systems are a rather artificial class of models. In real-

ity, canonical-dissipative systems, strictly according to their definition, do not exist. However there are many complex systems which have several properties in common with canonical-dissipative systems as

- the mechanical character of the motion, i.e. the existence of space and momentum, of quasi-Newtonian dynamics etc.,
- the support of the dynamics with free energy from internal or external reservoirs and the existence of mechanisms which convert the reservoir energy into acceleration.

If so, then the question arises, how systems near to having canonical-dissipative character can be treated by some kind of perturbation theory (see e.g. Haken, 1973; Ebeling, 1981).

6.5 Systems of particles coupled to Nose-Hoover thermostats

The nonequilibrium systems which we considered so far, were driven by negative friction, the stochastic effects were generated by an embedding into a thermal reservoir. This thermostat was assumed to be in equilibrium, what determined the passive friction and the noise. In connection with molecular-dynamical simulations, Nose' (1991) and Hoover (1988, 1998, 1999,

2001) developed a completely different class of thermostats, which found many applications (Hoover & Posch, 1996, Klages et al., 1999; Rateitschak et al., 2000). Because of the great interest in these systems, we will discuss now this new kind of imbedding.

The equations of motion for a Nose-Hoover thermostated particle on a plane confined in a parabolic well read (Hoover, 1998; 2001)

$$\frac{d}{dt}\boldsymbol{r} = \boldsymbol{v}\,;\ \frac{d}{dt}\boldsymbol{v} = -\gamma(t)\boldsymbol{v} - a\boldsymbol{r} \tag{6.61}$$

here γ is a variable friction

$$\frac{d}{dt}\gamma = \frac{1}{\tau^2}\left(\frac{v^2}{2T} - 1\right) \tag{6.62}$$

In the following we will use instead of the temperature T of the thermostat a characteristic velocity $v_0^2 = 2T$. By multiplication with v we get the energy balance

$$\frac{d}{dt}\left(\frac{v^2}{2} + \frac{ar^2}{2}\right) = -\gamma v^2 \tag{6.63}$$

The solutions for v^2 and γ are typically periodic functions. Let us now first consider the case $a = 0$. In Fig. 6.4 we have shown periodic trajectories in the plane v^2 vs. γ. The shape of the trajectories is a

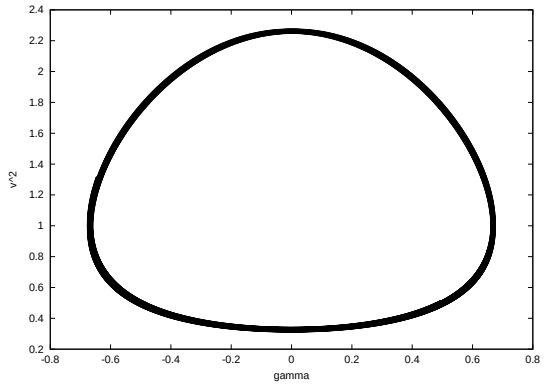

Fig. 6.4 Typical trajectories of free particles with a Nose-Hoover thermostat on the plane v^2 against γ.

hint to the existence of invariants of motion. By subtracting both equations and using the relation

$$\gamma = -\frac{d}{2dt}\log(v^2) \tag{6.64}$$

we find the following invariant of motion

$$\frac{d}{dt}\left(\frac{v^2}{2} - \frac{v_0^2}{2}\log\frac{v^2}{v_0^2} + \frac{\tau^2}{2}\gamma^2\right) = 0 \tag{6.65}$$

Therefore the trajectories are located on the surface

$$I_0 = \frac{v^2}{2} - \frac{v_0^2}{2}\log\frac{v^2}{v_0^2} + \frac{v_0^2}{2}\tau^2\gamma^2 = const. \tag{6.66}$$

The invariant of motion I_0 has the dimension of an energy (in our units $m = 1$). In Fig. 6.5 we have demonstrated the invariant I_0 and $v^2(t)$ as functions of time. There seems to be a relation between I_0 and Dettmann's Hamiltonian (Hoover, 2001). In Fig. 6.6 the invariant is represented in the plane v^2 against γ

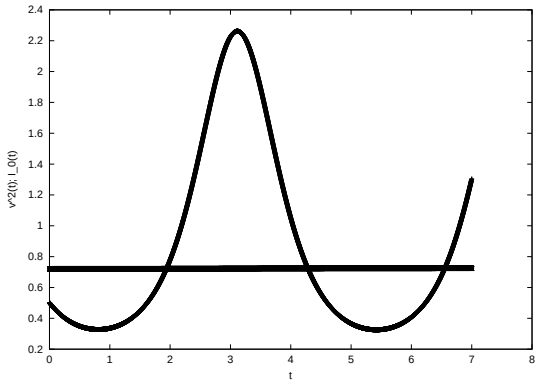

Fig. 6.5 Free particles in the NH-thermostat. We show the time dependence of $v^2(t)$ and the invariant I_0 according to a numerical integration.

for a noisy integration. The distribution function for a canonical ensemble is given by

$$f_0(\boldsymbol{v}) = C \exp\left(-\beta I_0(v,\gamma)\right). \tag{6.67}$$

In an approximation where $\beta v_0^2 \ll 1$ we find

$$f_0(\boldsymbol{v},\gamma) = C \exp\left(-\beta\frac{v^2}{2} - \beta\tau^2\frac{\gamma^2}{2}\right). \tag{6.68}$$

In the opposite case where $\beta v_0^2 \gg 1$ we get

$$f_0(\boldsymbol{v},\gamma) = C \exp\left(-\beta\frac{1}{4v_0^2}(v^2 - v_0^2)^2 - \beta\tau^2\frac{\gamma^2}{2}\right). \tag{6.69}$$

Finally we consider also the case of many particle $i = 1, 2, ..., N$ driven by thermostats through a time-dependent friction function

$$\frac{d}{dt}\boldsymbol{r}_i = \boldsymbol{v}_i\,;\ \frac{d}{dt}\boldsymbol{v}_i = -\gamma_i(t)\boldsymbol{v}_i - a\boldsymbol{r}_i + \sqrt{2D}\xi_i(t) \tag{6.70}$$

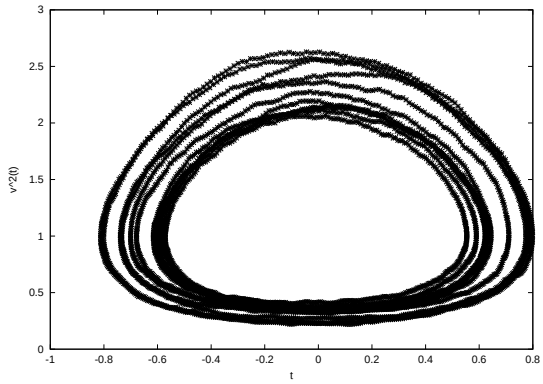

Fig. 6.6 The invariant of free particles in the NH-thermostat from a noisy integration.

In this case we may distinguish between two types of thermostats:
(i) individual thermostats defined by

$$\frac{d}{dt}\gamma_i = \frac{1}{\tau^2}\left(\frac{v_i^2}{2T} - 1\right) \tag{6.71}$$

(ii) collective thermostats with the same friction for all particles

$$\frac{d}{dt}\gamma = \frac{1}{\tau^2}\left(\frac{\Sigma\, v_i^2}{2NT} - 1\right) \tag{6.72}$$

Collective of thermostats (case (ii)) correspond in the case $\beta v_0^2 \gg 1$ approximately to a quasi-microcanonical ensemble in the dimension $d = 3N$. As shown by Klages et al. (1999) the distribution functions of this system may show central dips depending on the dimension d. We conclude this section by discussing the relations between Nose-Hoover thermostats and the depot models discussed in the previous section.

We introduce first a generalized depot model with dissipative forces $\boldsymbol{F}$ in the following form:

$$\boldsymbol{F}(e, \boldsymbol{v}) = \boldsymbol{v}(de^n - \gamma_0). \tag{6.73}$$

where e is the energy content of a depot and d is a conversion parameter. The first term expresses an acceleration in the direction of $\boldsymbol{v}$. The second term $\gamma_0 \boldsymbol{v}$ is the usual passive friction, which by assumption is connected with the noise by an Einstein relation $D = \gamma_0 kT/m$. We assume further that the Brownian particles are able to take up energy, which can be stored in the depot e. This internal energy can be converted into kinetic energy with a momentum dependent rate $de^n v^2$, which results in the acceleration in the direction of movement. The exponent n is free so far. The dissipative flow of energy into the mechanical systems is

$$\boldsymbol{v} \cdot \boldsymbol{F} = \boldsymbol{v}^2(de^n - \gamma_0). \tag{6.74}$$

If this energy flow comes from a depot with content e then we have the depot dynamics

$$\frac{de}{dt} = s(e) - de^n \boldsymbol{v}^2. \tag{6.75}$$

Here $s(e)$ is a function describing the support of the depot from an outside source. Now we specify the model: Asuming $n = 1$ and $s(e) = q - ce$ we come

back to the depot model studied in section 5.4. In order to find a Nose-Hoover-type dynamics we assume the exponent is $n = 1/2$ and postulate further the following balance of the depot (Ebeling & Röpke, 2003)

$$\frac{de}{dt} = q\sqrt{e} - ce - d\boldsymbol{v}^2\sqrt{e}. \tag{6.76}$$

Within this model we get in adiabatic approximation assuming $q > 0$ and requiring that the internal energy depot relaxes fast compared to the motion of the particle

$$\boldsymbol{F} = \boldsymbol{v}\left(\frac{d}{c}(q - dv^2) - \gamma_0\right). \tag{6.77}$$

Now, under the condition $((qd/c) - \gamma_0) > 0$, a root $v_0 > 0$ exists and we get a cubic law which corresponds to the Rayleigh friction law. We reformulate now the model in order to show the relation to NH-thermostats. Introducing a time-dependent friction variable $\gamma = \gamma_0 - d\sqrt{e}$ we find the "dissipative force"

$$\boldsymbol{F} = -\gamma(t)\boldsymbol{v}. \tag{6.78}$$

The friction variable satisfies the dynamic equation

$$\frac{d\gamma}{dt} = \frac{d}{2}\left(dv^2 - \frac{c}{d}\gamma - q + \frac{c}{d}\gamma_0\right). \tag{6.79}$$

By introducing here the new variables

$$v_0^2 = \frac{q}{d} - \frac{c\gamma_0}{d^2} \tag{6.80}$$

and

$$\tau^2 = \frac{2}{d^2 v_0^2}, \qquad \xi = \frac{c}{2} \tag{6.81}$$

we get the dynamics

$$\frac{d\gamma}{dt} = \frac{1}{\tau^2}\left(\frac{v^2}{v_0^2} - 1\right) - \xi\gamma, \tag{6.82}$$

where ξ is a dissipative constant. Assuming a special time evolution for ξ, we arrive at a dynamics discussed in section 7.10.3 of Hoover's book (Hoover, 2001). In the limit $\xi = 0$, i.e. $c = 0$ our system reduces to a conservative Nose-Hoover dynamics (Hoover, 1988, 1998, 2001; Klages et al., 1999). In the case $\xi = const > 0$ we find a dissipative Nose-Hoover dynamics. The corresponding Langevin equation contains a stochastic force. In order to simplify we assume that only the passive friction generates noise

$$D = \gamma_0 kT \tag{6.83}$$

$$\langle \xi_i(t) \rangle = 0\,; \;\; \langle \xi_i(t)\xi_j(t') \rangle = \delta(t - t')\delta_{ij} \tag{6.84}$$

In the simplest case of force-free particles the kinetic energy is a conserved quantity: $v^2 = const$. This

means, the system is canonical-dissipative. Consequently we are able to find exact solutions for the probability distribution following sections 5.3-5.4. For the dissipative Nose-Hoover dynamics we get the stationary distribution

$$f_0(v_1, v_2) = C \exp\left[-\alpha(v^2 - v_0^2)^2\right] \qquad (6.85)$$

with $\alpha = d/(4cD)$. We notice the close relation to Lorentz gas distributions (Klages et al.,1999; Rateitschak et al. , 2000). In conclusion we may say, that driving by velocity-dependent dissipative forces may have similar effects as driving by isokinetic thermostats.

6.6 Nonequilibrium distributions from information-theoretical methods

In this section we will show, how non-equilibrium distribution functions may be constructed by means of the information-theoretical methods which were introduced in section 4.4. This method which basically was developed by Gibbs and Jaynes (Jaynes, 1957; 1985). was further developed and applied to nonequilibrium situations by Zubarev (Subarev, 1976; Zubarev et al., 1996, 1997)). This information-theoretical method is of phenomenological character and connected with the maximum entropy approach. There is no reason to restrict the method to the equilibrium case. As stated by Jaynes (1957, 1985) the method should

work under much more general conditions. While in equilibrium we prescribe certain invariants of motion as e.g. energy, particle numbers etc. (see Section 4.4.) we have to look in nonequilibrium for more general observables. As we shall see, under non-equilibrium conditions, we should consider also macroscopic constraints due to the boundary conditions, as e.g. prescribed flows, angular momenta etc.. We consider quantities which may be represented as averages over the distribution and are prescribed in average by the conditions. This does not mean that these quantities are fixed, only the averages are prescribed and fluctuations around the means which are described by the distribution are possible. Then one constructs distribution functions which are compatible with the given averages. The free parameters in distribution function are found by maximizing the entropy of the distributions.

In the following we will pay special attention to the construction of non-equilibrium ensembles for systems with rotational modes, by using the Zubarev-formalism (Subarev, 1976; Zubarev, Morozov and Röpke, 1996, 1997). We will show in detail how the distributions are constructed if the angular integrals of motion are prescribed. Let us start now to explain the Jaynes-Zubarev approach to non-equilibrium sys-

tems. We consider an $N-$ particle system with the Hamiltonian:

$$H_S = \sum_i^N \frac{\boldsymbol{p}_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} V(\boldsymbol{r}_i - \boldsymbol{r}_j) \ . \qquad (6.86)$$

Including an embedding in surroundings, a heat bath, we have two additional terms in the total Hamiltonian:

$$H_{total} = H_S + H_B + H_{SB} \qquad (6.87)$$

here the bath is modeled by $H_B = H_B(Q,P)$, and the coupling by $H_{SB} = \Sigma_i^N V(\boldsymbol{r}_i, Q)$. Special cases are the isolated system with $H_{SB} = 0$ and external fields $V^{\rm ext}(\boldsymbol{r}_i)$ modeling traps.

Let us discuss now the form of the distribution functions. In non-equilibrium, in general, the linear "ansatz" used in the previous Chapter (**??**) is no more sufficient, since the means and the dispersion may be independent variables. In order to admit such situations we have to use quadratic function in the exponent of the distribution function. Let us assume that the mean values of the observables A_k and A_k^2 are given. In order to find the probability density under the constraints

$$A_k' = \langle A_k \rangle = \int dqdpA_k(q,p)\rho(q,p) \qquad (6.88)$$

$$A_k'' = \langle A_k^2 \rangle = \int dqdpA_k^2(q,p)\rho(q,p) \qquad (6.89)$$

we maximize the information entropy

$$\mathcal{H} = -\int dqdp\rho(q,p)\ln\rho(q,p) \tag{6.90}$$

under the given constraints. We define two m-component vectors $\lambda' = [\lambda'_1, ..., \lambda'_m]$ and $\lambda'' = [\lambda''_1, ..., \lambda''_m]$ of Lagrange-multipliers. Then the probability density that agrees with the given data $\mathbf{A}'$ follows from

$$\delta[\mathcal{H}+\sum_k \lambda'_k(A'_k-\int dqdpA_k(q,p)\rho(q,p))+\sum_k \lambda''_k(A''_k-\int dqdpA_k^2(q,p)\rho \tag{6.91}$$

This leads to

$$\rho(q,p) = Z^{-1}\exp[-\sum_k(\lambda'_k A_k(q,p) + \lambda''_k A_k^2(q,p)], \tag{6.92}$$

where the normalization factor, the so-called partition function, is now given by

$$Z(\lambda_1, ..., \lambda_m) = \int dqdp\exp[-\sum_k(\lambda'_k A_k(q,p)+\lambda''_k A_k^2(q,p))]. \tag{6.93}$$

The choice of the parameters should reflect the conditions (6.88) and (6.89).

The choice of the observables A_k describing the physical problem is not clear from the beginning. Candidates are the invariants of the dynamics and quantities which are prescribed by the boundary conditions. Among the invariant quantities the angular momentum is of special interest.

We will consider now this class of observables in more detail. The interest in a theory of rotational systems is due to the important role of rotations in nature. For example we mention the typical rotations of astrophysical objects as stars and planets, in macroscopic, mesoscopic and in atomic systems. In general one can say that most confined or selfconfined physical systems show rotational modes. In recent times finite Coulomb systems as quantum dots are in the center of interest (Bonitz et al., 2002; Dunkel et al., 2004).

In our context the $N-$ particle angular momentum is given as the sum of the momenta of the particles:

$$\boldsymbol{L}_N = \sum_i^N \boldsymbol{L}_i, \quad \boldsymbol{L}_i = \boldsymbol{r}_i \times \boldsymbol{p}_i \ . \tag{6.94}$$

Further $\boldsymbol{L}_N^2$ and higher powers of the angular momenta sometimes are of interest (see e.g. the theory of atoms and molecules). The time evolution of the angular momentum is given by:

$$\frac{d}{dt}\boldsymbol{L}_N = \frac{i}{\hbar}[H, \boldsymbol{L}_N] = \frac{i}{\hbar}[H_{SB}, \boldsymbol{L}_N] \ . \tag{6.95}$$

We will assume central forces, so that any change of the angular momentum is due to the "bath". If the coupling H_{SB} is absent or has rotational symmetry then the total angular momentum is a conserved

quantity. Alternatively we may prescribe the angular momentum by boundary conditions. The total angular momentum $\boldsymbol{L}_N$ is a conserved quantity, if the coupling H_{SB} is absent or has rotational symmetry. Alternatively we may prescribe it by boundary conditions. Let us assume that the average

$$\langle \boldsymbol{L}_N^n \rangle = \int d\Gamma \rho \boldsymbol{L}_N^n = const \tag{6.96}$$

for any given n is fixed. Then, we will postulate, that the distribution is a function of H_S and of $\boldsymbol{L}_N$

$$\rho = \rho(H_S, N, \boldsymbol{L}_N) \ . \tag{6.97}$$

The concrete form of the distribution is assumed to be determined by the expectation values. This may be a canonical distribution, but also any other forms of functional dependence are possible. Two cases are of special interest:
1) For rotating bodies of N particles which are only weakly coupled to an external heat bath and which otherwise are in internal equilibrium, the distribution is of particular simplicity. Assuming that conserved quantities H_N, N and $\boldsymbol{L}_N$ are the observables and that the corresponding Lagrange parameters are β, μ and $\boldsymbol{\omega}$, we find according to Section 4.4. an extended canonical Gibbs distribution (Landau & Lif-

shits, 1990).

$$\rho_{\rm eq} = \frac{1}{Z_{\rm eq}} \exp\left[-\beta(H_S - \mu N - \boldsymbol{\omega}\cdot\boldsymbol{L}_N)\right]. \quad (6.98)$$

here $\boldsymbol{\omega}$ is the angular velocity.
2) If the torque due to the surrounding bath is weak, then $\boldsymbol{L}_N$ is nearly conserved, it is a long-living mode of the system. In particular this is the case if the cluster and the surrounding have nearly spherical symmetry. Then $\boldsymbol{L}_N$, $\boldsymbol{L}_N^2$, etc. are quasi-conserved and should be included in the relevant distribution $\rho_{\rm rel}$ (Zubarev et al., 1996, 1997; Ebeling & Röpke, 2004). We may assume that several $n-$ order moments of the angular momentum are given at time t as e.g.

$$\langle L_N\rangle^t = \int d\Gamma\cdot\rho_{\rm rel}(t)L_N,$$

$$\langle L_N^2\rangle^t = \int d\Gamma\cdot\rho_{\rm rel}(t)L_N^2. \quad (6.99)$$

We assume further that the relevant distribution $\rho_{\rm rel}$ is again a generalized Gibbs distribution but including higher momenta

$$\rho_{\rm rel}(t) = \frac{1}{Z_{\rm rel}(t)} \exp\left[-\beta\left(H_S - \mu N - \sum_n \boldsymbol{\Omega}_n(t)\boldsymbol{L}_N^n\right)\right] \quad (6.100)$$

In this distribution in addition to β, μ, the free parameters $\boldsymbol{\Omega}_n$ appear, which characterize nonequilibrium quantities. The following step according to

Jaynes-Zubarev is to maximize the Gibbs entropy

$$S = \int d\Gamma \rho_{rel} \cdot \ln \rho_{rel} \tag{6.101}$$

under the given constraints (6.96). In this procedure the new parameters appear as the Lagrange multipliers $\boldsymbol{\omega}_{(n)}(t)$ and may be determined by the prescribed averages (6.96) as shown in detail e.g. in (Jaynes, 1957; Subarev, 1976; Zubarev et al., 1996). Of special importance for our problems is the case $n = 2$, i.e. the square of the angular momentum is given.
If the torque is weak, then the relaxation time of the angular momenta is quite long. An estimate of the relaxation time may be found also by linear response theory, which yields the expression (Zubarev et al.,1996)

$$\tau_L \propto \int_0^\infty dt \, \langle \left(\frac{d\boldsymbol{L}_N}{dt}\right)_t \left(\frac{d\boldsymbol{L}_N}{dt}\right)_{t=0} \rangle \, ,$$

The equilibrium correlation function may be evaluated by simulations or by analytical methods like perturbation expansions.
Among the quantities which may be prescribed by the surrounding, the kinetic energy is of special interest. Due to specific boundary conditions in some situations the individual kinetic energies are prescribed up to certain accuracy. For example, the interaction with a laser beam or with a surrounding plasma may

fix the kinetic energies of the individual particles T_i around some value given by the laser intensity

$$T_i = \frac{m_i}{2}\boldsymbol{v}_i^2 \simeq T_0 \ .$$

In a recent papers Trigger and Zagorodny have shown that the charged grains in a dusty plasma have a velocity distribution which is peaked around a characteristic velocity (kinetic energy) of the grains (Trigger and Zagorodny, 2002, 2003; Trigger, 2003).
As already mentioned, sometimes often the experimental conditions are such that the particles are driven to to a prescribed kinetic energy

$$\boldsymbol{v}_i^2(t) \rightarrow v_0^2$$

An example are charged grains in dusty plasmas (Trigger & Zagorodny, 2002, 2003, Trigger, 2003) or Coulomb clusters driven by a strong laser field. Due to the interaction with the surrounding, in the examples the "bath" is given by the plasma ions or the radiation field, the particles are accelerated to certain kinetic energy. In th is case we postulate that the distribution is of the following form

$$\rho_N(\boldsymbol{v}_1, ..., \boldsymbol{v}_N) = \Pi_{i=1}^N \tag{6.102}$$
$$\exp\left[-\alpha_v(\boldsymbol{v}_i^2 - v_0^2)^2\right]. \tag{6.103}$$

According to this distribution the most probable squared velocities (kinetic energies) are at the values v_0^2. Here

α_v is an appropriate parameter characterizing the dispersion. We denote this type of ensemble "isokinetic ensemble". This notation is borrowed from molecular dynamics, where Gaussian isokinetic ensembles play a big role (Hoover, 1988, 1998, 1999; Rateitschak et al., 2000).

A generalization are conditions fixing the individual energies H_i of the particles on the given value H_0. This leads to the Gaussian distributions

$$\rho_N(r_1, ...r_N, v_1, ..., v_N) = \Pi_{i=1}^N \tag{6.104}$$

$$\exp\left[-\alpha_H (H_i - H_0)^2\right] \tag{6.105}$$

In radially symmetric systems the driving to v_0^2 or H_0 implies for a special class of systems (an example will be given below) that $\boldsymbol{L}_i$ is also fixed to certain L_{i0}. This is due to internal connections between the invariants of motion. The existence of rotations means, that the symmetry with respect to all directions in space is broken, i.e correspondingly the distribution functions should be modified. Therefore we will consider also the distributions

$$\rho_N(L_1, ..., L_N) = \Pi_{i=1}^N \exp\left[-\alpha_L (\boldsymbol{L}_i - L_{i0})^2\right] \tag{6.106}$$

A different 'ansatz' is based on the invariant $H - \boldsymbol{\Omega} \cdot \boldsymbol{L}$

which is a kind of internal Hamiltonian and reads

$$\rho_0(q_1...q_f p_1...p_f) = Z^{-1}(\Omega) \quad (6.107)$$

$$\exp\left(-\alpha_1(H - E_0)^2 - \alpha_2(H - \boldsymbol{\Omega}\cdot\boldsymbol{L})\right). \quad (6.108)$$

This way we may prescribe the most probable value of the total energy and of the internal energy separately by the choice of α_1, α_2.
More general forms of the distributions are Gaussian distributions centered around the prescribed invariants of motion

$$\rho_0(q_1...q_f p_1...p_f) = const.\Pi_{k=0}^{s} \quad (6.109)$$

$$\exp\left(-c_k\frac{(I_k(q_1...q_f, p_1...p_f) - I_k)^2)}{2D}\right). \quad (6.110)$$

However as we have shown above, there is no guaranty that the distributions constructed in this way already have the correct physical symmetry. This has to be checked in every concrete case. In the limit of very strong driving the probability reduces to a kind of microcanonical ensemble corresponding to the shell defined by $I_0, I_1, ..., I_s$ with a constant probability density on the shell. Let us discuss now in brief the physical meaning and symmetry properties of probability distributions which express prescribed angular momenta. Where is the probability concentrated in the phase space? We consider as a simple

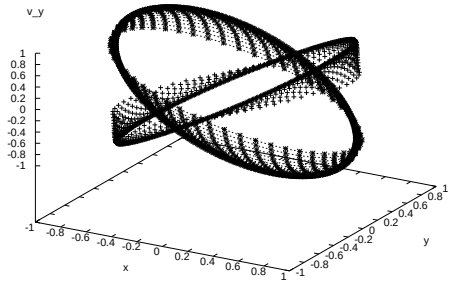

Fig. 6.7
Typical distribution of a rotating 2-d particle with fixed angular momentum $\boldsymbol{L}^2 = L_0^2$. *The two possible values of the angular momentum select two tires on the sphere* $H = const.$. *We see a projection of the 4-dimensional phase on the* $x - y - v_y -$ *space.*

case of a particle rotating on a 2-dimensional plane, i.e. we have a 4-dimensional phase space (a physical realization was considered already in Section 5.1 and will be studied in more detail in Chapter 12). Then fixation of the most probable value of the total energy $H = E_0$ defines the surface of a sphere (or a cylinder if the kinetic energy is prescribed) in the 4-dimensional space:

$$\frac{m}{2}(v_1^2 + v_2^2) + \frac{m}{2}\omega_0^2(x_1^2 + x_2^2) = E_0$$

In order to characterize the two rotating states we introduce two non-negative invariants of motion

$$J_+ = H - \omega_0 L = \frac{m}{2}(v_1 + \omega_0 x_2)^2 + \frac{m}{2}(v_2 - \omega_0 x_1)^2 \tag{6.111}$$

and

$$J_- = H + \omega_0 L = \frac{m}{2}(v_1 - \omega_0 x_2)^2 + \frac{m}{2}(v_2 + \omega_0 x_1)^2. \tag{6.112}$$

The condition $J_+ = 0$ characterizes rotations with positive angular momentum ($L \simeq H_0/\omega_0$) and the condition $J_- = 0$ characterizes rotations with negative angular momentum ($L \simeq -H_0/\omega$). Geometrically $J_\pm = 0$ define two surfaces in the 4-dimensional space which intersect the sphere $H = H_0$ in two circles representing the trajectories of the rotating states (see Fig. 6.7). For the corresponding probabilities we may assume the Gaussian distribution with two free parameters

$$\rho(\mathbf{r}, \mathbf{v}) = C \exp\left[-\alpha_H (H - H_0)^2\right] \tag{6.113}$$

$$\left[\exp(-\mu J_+) + \exp(-\mu J_-)\right]. \tag{6.114}$$

We note that for the special choice $\mu = 2\alpha_H H_0$ we may bring this to the more special form

$$\rho(\mathbf{r}, \mathbf{v}) = C' \exp\left[-\frac{\mu}{2H_0}(H^2 - H_0^2)\right] \tag{6.115}$$

$$\left[\exp(+\mu\omega_0 L) + \exp(-\mu\omega_0 L)\right] \tag{6.116}$$

This way the probability will be concentrated on two tires in the phase space.

Let us summarize our findings: We used in this section the method of generalized Gibbs distributions

(Gibbs, 1902; Landau & Lifshits, 1990) and in particular the Zubarev method for constructing relevant distributions (Subarev, 1976; Zubarev et al., 1996, 1997). These methods are of phenomenological character and connected with the maximum entropy approach. We repeat the basic assumptions: Due to the boundary conditions certain averages as e.g. here the angular momentum L_N or L_N^2 are prescribed. This does not mean that the quantities are fixed, only the averages or the most probable values are prescribed and fluctuations around these values which are described by the distribution are possible. The distribution function is found by maximizing the entropy of distributions which fulfill the given constraints.