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Rouslan L. Stratonovich

Nonlinear Nonequilibrium Thermodynamics I

Linear and Nonlinear
Fluctuation-Dissipation Theorems

With 26 Figures

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Preface

This book gives the first detailed coherent treatment of a relatively young branch of statistical physics – nonlinear nonequilibrium and fluctuation–dissipative thermodynamics. This area of research has taken shape fairly recently: its development began in 1959. The earlier theory – linear nonequilibrium thermodynamics – is in principle a simple special case of the new theory. Despite the fact that the title of this book includes the word “nonlinear”, it also covers the results of linear nonequilibrium thermodynamics. The presentation of the linear and nonlinear theories is done within a common theoretical framework that is not subject to the linearity condition.

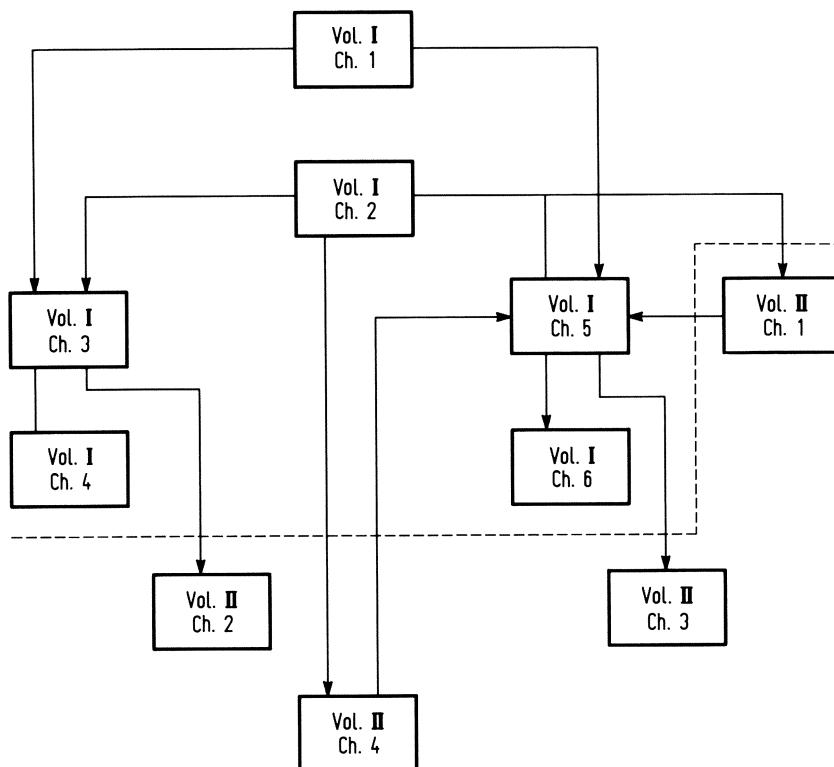
The author hopes that the reader will perceive the intrinsic unity of this discipline, and the uniformity and generality of its constituent parts. This theory has a wide variety of applications in various domains of physics and physical chemistry, enabling one to calculate thermal fluctuations in various nonlinear systems.

The book is divided into two volumes. Fluctuation–dissipation theorems (or relations) of various types (linear, quadratic and cubic, classical and quantum) are considered in the first volume. Here one encounters the Markov and non-Markov fluctuation–dissipation theorems (FDTs), theorems of the first, second and third kinds. Nonlinear FDTs are less well known than their linear counterparts.

Advanced problems are considered in the second volume. Among them the reader will find (1) the non-Markov generating equation from which FDTs of all degrees of nonlinearity can easily be obtained; (2) nonequilibrium thermodynamics of open systems; (3) FDTs for coherent waves interacting with a physical body (these are sometimes called the Kirchhof-type FDTs); and (4) the problem of obtaining the Markov process and Markov FDT from Hamiltonian dynamics.

The connection and interdependence of the material in the various chapters are illustrated in the diagram on the next page.

The first volume of the book begins with two introductory chapters. Chapter 1 gives some preliminary concepts of nonequilibrium thermodynamics and a historical outline of its development. Chapter 2 presents some useful information, in particular a number of useful concepts of probability theory and some important facts of equilibrium thermodynamics. The reader might possibly find the presentation in this chapter somewhat unusual. The important parts of the theory are the non-equilibrium thermodynamics of Markov systems, i.e. systems with no after-effect (Chaps. 3 and 4), and the nonequilibrium thermodynamics of arbitrary systems in which an after-effect is allowed (Chaps. 5 and 6). In the absence of an after-effect a system is described by phenomenological equations that can be reduced to a set of memoryless first-order equations. These equations are the starting point for the



Markov theory. A set of functions – admittances or impedances –, which describe the response of the system to variable external input forces, are the starting point for the non-Markov, i.e. more general nonequilibrium thermodynamics.

The level of rigor and mathematical techniques in the book are those generally accepted in theoretical physics (see, e.g., Course of Theoretical Physics by L.D. Landau and E.M. Lifshits).

The book will appeal to theoretical physicists and applied scientists. The latter may wish to ignore derivations of some universal relations and simply utilize them to handle problems of interest to them. The theoretical treatment is supported by numerous illustrative examples and applications of the general results to a variety of electrical, thermal, mechanical and chemical systems. It is shown that the most complete analysis of specific systems is achieved by the fusion of the Markov and non-Markov techniques of nonequilibrium thermodynamics.

The bibliography, especially in relation to linear nonequilibrium thermodynamics and the nonequilibrium thermodynamics of open systems, does not claim to be exhaustive.

Chapters 1–5 were translated by Mrs. V.V. Stratonovich, and Chap. 6 was translated by Mr. A.P. Repjev.

I would like to thank Professor H. Haken for his suggestion to publish this book in the Springer Series in Synergetics. I am grateful to the first reader of the book Professor Yu. Klimontovich for his useful comments. I also thank Angela Lahee for her careful editing of the manuscript.

Moscow, June 1992

R.L. Strattonovich

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1. Introduction

1.1 What Is Nonlinear Nonequilibrium Thermodynamics?

There appears to be general consensus on what equilibrium thermodynamics is. However, regarding what nonlinear nonequilibrium thermodynamics is and what topics it covers, authorities are divided at present. We are not going to dwell on these disagreements, which are adequately reflected in the literature, but simply state our opinion on the subject.

First of all, what is “thermodynamics” in general? We take it to refer to a science that establishes universal relations (pertaining to thermal and other processes in statistical physics) between macroscopically measurable physical quantities. Let us take, for instance, the well-known thermodynamic relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \quad (1.1.1)$$

where p is the pressure, V is the volume and T is the temperature, all these quantities being macroscopically measurable. The entropy S , although not measurable directly, is related to measurable quantities by the well-known equation $dS = dQ/T$. Equation (1.1.1) is universal in the sense that it holds irrespective of the specific form of the Hamiltonian function describing the system at hand. This relation, just as other similar relations for higher derivatives, follows from the equations

$$S = -\frac{\partial F(T, V)}{\partial T}, \quad p = -\frac{\partial F(T, V)}{\partial V}. \quad (1.1.2)$$

In the general case, these can be written as

$$A_\alpha = -\frac{\partial F(a)}{\partial a_\alpha}, \quad (1.1.3)$$

where F is the free energy and a_α is a set of external parameters. The internal parameters A_α and the external parameters a_α are macroscopically measurable. The free energy $F = U - TB$ can also be treated as measurable. Therefore, equations (1.1.3) are thermodynamic relationships.

Let us now take the equation

$$w(B) = \text{const} \cdot \exp[-F(B)/kT], \quad (1.1.4)$$

where B represents random internal parameters. It relates a macroscopically

measurable function – the free energy – to another macroscopically measurable function: the probability density $w(B)$ of fluctuations of B . Of course, to observe the small thermal fluctuations of parameters one will need some amplifying system, but this system will be macroscopic; therefore, the measurements of fluctuations in general and the density $w(B)$ in particular are macroscopic. Consequently, (1.1.4) can be regarded as a thermodynamic relation in the sense mentioned above.

We will now turn to the well-known equation relating the free energy to the statistics integral

$$F = -kT \ln \int \exp[-\mathcal{H}(q, p)/kT] dq dp . \quad (1.1.5)$$

As noted, the free energy is a macroscopically measurable quantity, but the Hamiltonian function $\mathcal{H}(q, p)$ for systems dealt with in statistical physics, which contain an enormous number of molecules (of the order of the Avogadro number), is an abstract concept, a purely mental construct. It can by no means be thought of as macroscopically measurable. Therefore, strictly speaking, (1.1.5) cannot be treated as a thermodynamic relation in the sense mentioned earlier. It can only be referred to statistical thermodynamics understood in a context wider than that defined earlier.

Until now we have dealt with equations of the equilibrium theory. What has been said above is also true for the nonequilibrium theory, which takes into account time variations of internal parameters. Nonequilibrium thermodynamics starts off with the macroscopic phenomenological equations

$$dA_\alpha/dt = f_\alpha(A), \quad \alpha = 1, 2, \dots , \quad (1.1.6)$$

which describe the time variation of the macroscopic parameters $A = (A_1, A_2, \dots)$. Derivation of the functions $f_\alpha(A)$ from the Hamiltonian function is no concern of thermodynamics understood in the narrow sense, nor is the calculation of free energy by using this function. But the well-known Onsager relations

$$\partial f_\alpha / \partial X_\beta = \partial f_\beta / \partial X_\alpha \quad \text{for } A = A^0 \quad (1.1.7)$$

fall fully in the realm of nonequilibrium thermodynamics. Here A^0 represents the equilibrium values of the parameters A ; $X = X(A)$ are thermodynamic forces given by $X = -\partial S(A)/\partial A$. In fact, (1.1.7) establishes a relation between the quantities $\partial f_\alpha / \partial X_\beta$, which are measurable since $f_\alpha(A)$, just as the curves $A_\alpha(t)$, can be measured macroscopically. Further, this relation is universal since it remains unchanged when the Hamiltonian function changes.

No doubt, the fluctuation-dissipation theorem also is a part of thermodynamics in the above-mentioned narrow sense since correlators and the response of a macrosystem to a macroforce can be measured macroscopically. But the calculation of transport coefficients (linear and nonlinear) from the accepted law of microinteraction of molecules is no concern of nonequilibrium thermodynamics. Also, thermodynamics does not deal with the derivation and use of some specific master equation, say the Boltzmann equation, since it is only valid for certain (short-range) forces of intermolecular interaction. For other forces another equation may hold instead, e.g. the Vlasov equation. Moreover, the Boltzmann equa-

tion is written for the distribution of microscopic velocities (molecular velocities), whereas thermodynamic relations must solely involve macroscopic quantities.

Now we can answer the question what the subject of thermodynamics is: thermodynamics establishes universal relations and formulas involving macroscopically measurable quantities. The universality of these relationships is worth stressing there. Changing the Hamiltonian function of a system and its properties, e.g. the concentration of molecules, and their interaction potential, will change the quantities and functions related by a thermodynamic equation, whereas the relationships itself will remain unchanged. The subject matter of nonequilibrium thermodynamics is the derivation of the universal relations involving macroscopic time characteristics of the system, i.e. the quantities characterizing the temporal behaviour of the system.

1.1.1 Foundations of Nonequilibrium Thermodynamics

The universal nature of the equations of nonequilibrium thermodynamics stems from the fact that they are derived from fairly general premises. We will take a look at them now.

1. It is only natural that the results of nonequilibrium thermodynamics derive from some important results of equilibrium thermodynamics. Among them are formulas [one of them (1.1.4)] according to which the one-time equilibrium probability density of internal parameters is expressed in terms of entropy or free energy, which are the functions of internal parameters. This important premise of nonequilibrium thermodynamics – the validity of equations giving an equilibrium distribution – can be called the “principle of dynamic equilibrium”.

2. Another important foundation is the principle of time reversibility, i.e. the invariance of statistical characteristics of a fluctuational process $B(t)$ under time reversal. This follows from the time reversibility of microprocesses, which is a consequence of the invariance of the Hamiltonian function under time reversal. This invariance is given by

$$\mathcal{H}(q, -p) = \mathcal{H}(q, p). \quad (1.1.8)$$

If the principle of time reversibility is invalid, then the number of useful relations of nonequilibrium thermodynamics is reduced drastically, and so the theory becomes much poorer.

3. A third postulate is the law of causality, which gives rise to a number of equations such as

$$\delta A(t_1)/\delta h(t_2) = 0, \quad \text{for } t_2 > t_1, \quad (1.1.9)$$

where $A(t)$ represents averaged internal parameters due to the action of non-constant thermodynamic forces $h(t')$. The law can also be applied in a wider context; namely, as a postulate leading to the inferences such as: (i) if a system includes no dissipative elements, no fluctuational forces will be engendered within it; or (ii) if a system has no nonlinear dissipative elements, then it has no sources of non-Gaussian thermal fluctuations.

4. There are problems in which special forms of symmetry turn out to be of use, e.g. the symmetry under three-dimensional rotations.

It will be recalled that it is the time reversibility that underlies the derivation of Onsager's reciprocal relations. It is also necessary to derive the quadratic fluctuation-dissipation theorem. The principles of dynamic equilibrium and time reversibility enable the global or generating equations to be established, which yield relations for various degrees of nonlinearity: linear, quadratic, cubic, etc.

1.1.2 What Nonequilibrium Results Are Discussed in This Book?

The term "nonlinear" in the title of the book is an indication of the main direction, but it does not suggest that linear nonequilibrium thermodynamics is totally excluded from the consideration. The linear thermodynamic relations are treated as a simple special case, the linear and nonlinear relations being derived from the general theory.

We will now summarize the basic results of linear nonequilibrium thermodynamics:

1. Onsager–Casimir reciprocal relations and their generalization to systems with after-effect (the reciprocal relations of the non-Markov theory)
2. Linear fluctuation-dissipation theorems (FDTs) or fluctuation-dissipation relations (FDRs)
3. Linear H -theorems

The following are the main results of the nonlinear theory:

1. Global or generating equations, Markov and non-Markov.
2. Nonlinear FDTs, or rather FDRs, that follow from the above equations.
3. General (nonlinear) H -theorems.
4. Results concerning the way of inclusion of external forces into the phenomenological equation without forces.

There are also some results for open systems, but we are not going to dwell on them here.

Unlike linear nonequilibrium thermodynamics, its nonlinear counterpart concentrates on fluctuation-dissipation relations connecting nonequilibrium characteristics of a system with fluctuational (equilibrium or nonequilibrium) characteristics. Purely dissipative results are few. This is because important non-fluctuational results of the linear theory, such as the reciprocal relations of the Onsager–Casimir type written for a relaxation process, cannot be generalized to the nonlinear region. If there were reciprocal relations of the type (1.1.7) for higher derivatives, then we would have a formula, similar to (1.1.3), which would suggest that phenomenological relaxation has potential nature:

$$dA_\alpha/dt = - \partial V(X)/\partial X_\alpha \quad \text{for } X = X(A), \quad (1.1.10)$$

where $V(X)$ is a certain nonequilibrium potential. According to (1.1.7), equation (1.1.10) holds for the quadratic potential

$$V(X) = \sum v_{\alpha\beta} X_\alpha X_\beta. \quad (1.1.11)$$

But if higher powers of X are taken into account, (1.1.10) cannot be proved. Moreover, there are examples where it does not hold. Even the Onsager relations (1.1.7) hold not always, but only when all A have the same time parity (i.e. either all remain unchanged or all change sign under time reversal).

Purely nonfluctuational (not concerned with fluctuational characteristics) results of the nonlinear domain of nonequilibrium thermodynamics are not many. These are:

1. Nonlinear H -theorems and related theorems.
2. Results associated with the inclusion of external forces into the nonfluctuational phenomenological equation (Sect. 5.5.8).
3. Relations determining the magnitude of weak (of the order of kT) internal thermodynamic forces appearing in quadratic dissipative elements of a system to counteract the detection of fluctuations of fluxes. If in such a system quadratic dissipative elements have different temperatures, these forces may give rise to relatively small nonfluctuational fluxes in the system.

But most equations are concerned both with dissipative and with fluctuational characteristics of the processes.

1.1.3 Distinguishing Features of Nonlinear Nonequilibrium Thermodynamics

It is to be noted that the relations of nonequilibrium thermodynamics permit two versions: the kT -version and the k -version. This duality underlies the theory: even in equilibrium thermodynamics there are two main distributions, the micro-canonical distribution and the canonical Gibbs distribution. In the book we will frequently stress the fact that two versions of an equation are possible. The kT -version will be taken to be the main one, and the treatment will begin with it. This choice is accounted for by the fact that the first law of thermodynamics is conventionally written in the kT -version and the ordinary linear fluctuation-dissipation theorem is also formulated in the kT -version, although it also permits formulation in the k -version.

In terms of the kT -version, the forces conjugate to A_α are introduced by the expression $x_\alpha = \partial F(A)/\partial A_\alpha$ and, instead of (1.1.7), we have

$$\frac{\partial f_\alpha}{\partial x_\beta} = \frac{\partial f_\beta}{\partial x_\alpha} \quad \text{for } A = A^0. \quad (1.1.12)$$

It is worth noting the intrinsic unity of the theory, the uniformity of various parts of nonequilibrium thermodynamics and the similarity between some of its features and those of equilibrium thermodynamics. Take, for example, the thermodynamic forces conjugate to A_α . These have first appeared in equilibrium thermodynamics as external parameters a_α . Then, in the Markov nonequilibrium thermodynamics appear the forces x_α , which are in essence nonequilibrium shifts $a_\alpha - a_\alpha^0$ (a_α^0 represent the equilibrium values). Lastly, the non-Markov nonequilibrium thermodynamics deals with the forces $h_\alpha(t)$ that have the same meaning as x_α , but now vary with time.

Also remarkably uniform and parallel are the various fluctuation-dissipation relations (FDRs) from different parts of nonequilibrium thermodynamics: the Markov and non-Markov FDRs of various kinds.

A characteristic feature of nonequilibrium thermodynamics to be discussed in the book is the fact that, like equilibrium thermodynamics, it includes both exact formulas and somewhat simplified asymptotic formulas that hold for large, i.e. macroscopic, systems. In other words, the latter are justified by the smallness of the Boltzmann constant. For example, in equilibrium thermodynamics the exact formula (2.2.86), which relates the free energies $F(a)$ and $F_0(A)$, for large systems can be replaced by the approximate formula (2.2.95), which relates the above functions by the Legendre transformation. In nonequilibrium theory the exact formula (3.1.32) for $V(y, B)$ and $R(y, x)$ for large systems can be replaced by the asymptotic formula (3.1.37). Apart from exact FDRs, asymptotic FDRs of varying accuracy are possible.

1.2 Early Work on Nonlinear Nonequilibrium Thermodynamics

Nonlinear nonequilibrium thermodynamics is a relatively young area of research in statistical physics. Although the linear relations – the Nyquist formula and the Onsager relation – were first derived in 1928 and 1931, respectively, the nonlinear relations were not obtained until much later. We will now only mention some works on nonlinear part of nonequilibrium thermodynamics.

The pioneering work was that of *Bernard* and *Callen* [1.1] in 1959. Among other results, Bernard and Callen found the way in which admittance in the quantum case is expressed through commutators of operators of internal parameters. They also attempted to work out one of the quadratic fluctuation–dissipation relations of the second kind; namely, to obtain the derivative of twofold moment with respect to external force in terms of quadratic admittance. The resulting expression turned out to be wrong, however, since it did not include a term with time conjugation.

A second contribution was made by *Stratonovich* [1.2] in 1960. He derived the two-time generating equation of the non-Markov theory; namely, the equation for step-driven processes.

In 1962, in a work [1.3] on the Markov nonlinear nonequilibrium thermodynamics the principle of time-reversal invariance was first used to obtain the results in nonlinear nonequilibrium theory. The nonlinear Markov FDRs [Ref. 1.3, equations (17) and (18)] were first derived and, moreover, an attempt was made to obtain more powerful results by imposing restrictions on generality; namely, to obtain the entire Markov operator from the phenomenological relaxation equations. The results of [1.3] hold for time-even internal parameters.

In 1967 a study [1.4] of the Markov FDRs was carried out. For time-even parameters the complete set of three-subscript (quadratic) and four-subscript (cubic) FDRs was obtained. And in [1.5] the three- and four-subscript FDRs for internal parameters having arbitrary time parity were derived. In 1970 [1.6] the nonlinear Markov FDRs were applied to work out the correlators of thermal noise in circuits including nonlinear resistances.

In parallel with the development of the Markov nonlinear nonequilibrium thermodynamics, the non-Markov theory was becoming established. In 1968 *Efremov* [1.7] proved the non-Markov quadratic fluctuation–dissipation theorem. In other words, he obtained in the quantum case two quadratic FDRs of the second kind. In 1970 the derivation of the quadratic FDRs of the second kind was simplified; their representation was made more rational, and it was also proved that there exist no cubic FDRs that would enable all the four-subscript functions to be completely expressed in terms of cubic admittance [1.8]. In other words, it was shown that the four-subscript functions have dissipationally undeterminable parts.

This concludes our short historical sketch of the first decade of the development of the nonlinear part of the nonequilibrium thermodynamics. Further references are to be found in respective chapters.

1.3 Some Particular Problems and Their Corresponding FDRs: Historical Aspects

1.3.1 Einstein's Problem: Determination of the Diffusion Coefficient of a Brownian Particle

In 1905 *Einstein* [1.9] made the first step in the direction of creating the theory of Brownian motion, i.e. he determined the diffusion coefficient D of a Brownian particle; D was expressed in terms of the particle mobility or in terms of the friction constant. The mobility μ is the inverse of the friction constant and is defined as a proportionality factor between the external force F acting on the particle and its mean velocity: $\langle v \rangle = \mu F$. Obviously, μ is the dissipative characteristic of the particle. The diffusion coefficient D may be regarded as a fluctuational characteristic according to the well-known formula

$$\langle (x - x_0)^2 \rangle = 2Dt . \quad (1.3.1)$$

Therefore, the relation obtained by Einstein is the special fluctuation–dissipation relation and, historically, the first one.

Let us give the derivation of this relation. We assume that the force F is directed along the x -axis. As a result of its action there occurs a flow of Brownian particles along this axis. The number of particles crossing unit area per unit time is equal to μFn , where n is the concentration, i.e. the average number of particles per unit volume. Besides, there exists a flow of particles which is caused by diffusion. Because of diffusion the number of particles crossing unit area per unit time is equal to $-D \partial n / \partial x$. When the dynamic equilibrium is established, the total flow is equal to zero, i.e.

$$\mu Fn - D \partial n / \partial x = 0 . \quad (1.3.2)$$

Further, the condition of force equilibrium must be fulfilled. Let us consider a layer $(x, x + \Delta x)$ having an area S . This layer is acted upon by pressure forces $p(x)S$ from

one side and $-p(x + \Delta x)$ from the other side. In the equilibrium state the resultant force $[p(x) - p(x + \Delta x)]S$ must be equal to the sum of external forces acting on particles in the layer; the number of particles is equal to $nS\Delta x$. As a result, we obtain

$$FnS - \frac{p(x + \Delta x) - p(x)}{\Delta x} S = 0 .$$

Hence, in the limit $\Delta x \rightarrow 0$ we find $Fn - \partial p / \partial x = 0$. Here p is the partial pressure caused by Brownian particles (the concentration of solvent particles and the corresponding pressure are assumed to be constant in x). This partial pressure is defined by the formula of ideal gas: $p = kTn$. Therefore,

$$Fn - kT \partial n / \partial x = 0 . \quad (1.3.3)$$

Comparing (1.3.2) with (1.3.3), we obtain the desired relation

$$D = kT\mu . \quad (1.3.4)$$

Einstein supposed that the particles were round and used the Stokes formula $\mu = (6\pi R\eta)^{-1}$ for describing the mobility. Here R is the particle radius and η is the viscosity.

Note that (1.3.3) is equivalent to the formula $d \ln(n) = (kT)^{-1} F dx$, which gives the Boltzmann distribution

$$\begin{aligned} n(x) &= \text{const} \cdot \exp \left(-\frac{1}{kT} \int_0^x F(x') dx' \right) \\ &= \text{const} \cdot \exp \left(-\frac{U(x)}{kT} \right) \end{aligned} \quad (1.3.5)$$

[$U(x)$ is the potential corresponding to the force $F(x)$]. Further, the equation $G = \mu Fn - D \partial n / \partial x$, which defines the total flow of Brownian particles, leads to the equation

$$\dot{n} = -\frac{\partial G}{\partial x} = \mu \frac{\partial}{\partial x} \left(\frac{\partial U}{\partial x} n \right) + D \frac{\partial^2 n}{\partial x^2} . \quad (1.3.6)$$

Hence, in the equilibrium case we have

$$\mu \frac{\partial}{\partial x} \left(\frac{\partial U}{\partial x} n \right) + D \frac{\partial^2 n}{\partial x^2} = 0 . \quad (1.3.7)$$

Substituting (1.3.5) into (1.3.7), we again obtain (1.3.4). Thus, using (1.3.6) (i.e. the special case of the Fokker–Planck equation) and the Boltzmann distribution is equivalent to Einstein's reasoning.

1.3.2 A Second Problem: Determination of the Intensity of a Random Force Acting on a Brownian Particle

An important step in creating the theory of Brownian motion was made by Ornstein in 1927 [1.10]. The intensity constant of the random force $F(t)$ entering

into the Newton equation was found. In the one-component case this equation has the form

$$m\dot{v} = -\beta v + F(t), \quad (1.3.8)$$

where $-\beta v = -\mu^{-1}v$ is the frictional force. The intensity constant is defined by the formula

$$K = \int_{-\infty}^{\infty} \langle F(t)F(t') \rangle dt'. \quad (1.3.9)$$

Ornstein assumed that the correlation time of the random force was very short. By using the Dirac δ -function this assumption can be written as

$$\langle F(t)F(t') \rangle = K\delta(t - t'). \quad (1.3.10)$$

We see that (1.3.10) conforms with (1.3.9). The assumption (1.3.10) is equivalent to the assumption that $v(t)$ has Markov properties.

The solution of (1.3.8) is easily found:

$$v(t) = \exp\left[-\frac{\beta}{m}(t - t_0)\right]v(t_0) + \frac{1}{m} \int_{t_0}^t \exp\left[-\frac{\beta}{m}(t - \tau)\right]F(\tau) d\tau. \quad (1.3.11)$$

Squaring both sides of the last equation and averaging the results, we find at $t_0 = -\infty$

$$\langle v^2(t) \rangle = \frac{1}{m^2} \int_{-\infty}^t \int_{-\infty}^t \exp\left[-\frac{\beta}{m}(2t - \tau - \sigma)\right] \langle F(\tau)F(\sigma) \rangle d\tau d\sigma. \quad (1.3.12)$$

Substituting (1.3.10) into (1.3.12), after integration we have

$$\langle v^2 \rangle = \frac{K}{2\beta m}. \quad (1.3.13)$$

But the equation $\langle v^2 \rangle = kT/m$ is valid because of equipartition law. Hence, (1.3.13) gives

$$K = 2kT\beta = 2kT\mu^{-1}. \quad (1.3.14)$$

The force $F = \{F_\alpha\}$ is a vector in the many-component case, and instead of (1.3.10) the formula $\langle F_\alpha(t)F_\beta(t') \rangle = K\delta_{\alpha\beta}\delta(t - t')$ is valid for the same K .

The relation (1.3.14) connecting the fluctuational characteristic K with the dissipative one is, historically, the second special fluctuation–dissipation relation (FDR). In [1.11, 12] it was also obtained by another method, i.e. by using the Fokker–Planck equation written for velocity probability density.

1.3.3 The More General Linear Markov FDR

From the modern point of view formulas (1.3.4, 14) are the consequences of the general linear Markov FDR. We suppose that the many-component Markov process $\{B_\alpha(t)\}$ is given. It is described by the Fokker–Planck equation

$$\frac{\partial w(B)}{\partial t} = \frac{\partial}{\partial B} (d_{\alpha\beta} B_\beta w) + \frac{1}{2} K_{\alpha\beta} \frac{\partial^2 w}{\partial B_\alpha \partial B_\beta} \quad (1.3.15)$$

($d_{\alpha\beta}$ and $K_{\alpha\beta}$ are independent of B and t ; the summation over repeated subscripts is understood). We also suppose that (1.3.15) has a stationary solution. It can be proved that the stationary distribution is Gaussian:

$$w(B) = \text{const} \cdot \exp(-\frac{1}{2} a_{\alpha\beta} B_\alpha B_\beta) \quad (a_{\alpha\beta} = a_{\beta\alpha}). \quad (1.3.16)$$

Here the mean values $\langle B \rangle$ are equal to zero; this is connected with the definite choice of the coordinate origin in B -space. As is well known from the theory of Gaussian random variables, the second moment matrix $\langle B_\alpha B_\beta \rangle$ is related to the matrix $a_{\alpha\beta}$ entering into (1.3.16) by a simple formula,

$$\|\langle B_\alpha B_\beta \rangle\| = \|a_{\alpha\beta}\|^{-1}, \quad (1.3.17)$$

i.e. the matrix $\langle B_\alpha B_\beta \rangle$ is the inverse of $a_{\alpha\beta}$.

In the case of the stationary distribution, which does not change in time, we obtain from (1.3.15)

$$2 \frac{\partial}{\partial B_\alpha} (d_{\alpha\beta} B_\beta w) + K_{\alpha\beta} \frac{\partial^2 w}{\partial B_\alpha \partial B_\beta} = 0. \quad (1.3.18)$$

Substituting (1.3.16), we obtain after differentiation

$$2d_{\alpha\alpha} - K_{\alpha\beta} a_{\beta\alpha} + (K_{\alpha\beta} a_{\alpha\gamma} a_{\beta\delta} - 2d_{\alpha\gamma} a_{\alpha\delta}) B_\gamma B_\delta = 0. \quad (1.3.19)$$

In order that this equation be satisfied for arbitrary B_γ , the quadratic form and the difference $2d_{\alpha\alpha} - K_{\alpha\beta} a_{\beta\alpha}$ must be zero, i.e.

$$\sum_{\alpha\beta} K_{\alpha\beta} a_{\beta\alpha} = \sum_\alpha 2d_{\alpha\alpha}. \quad (1.3.20)$$

The quadratic form is zero provided

$$K_{\alpha\beta} a_{\alpha\gamma} a_{\beta\delta} = a_{\delta\alpha} d_{\alpha\gamma} + a_{\gamma\alpha} d_{\alpha\delta}. \quad (1.3.21)$$

In particular, from (1.3.21) we get

$$K_{\alpha\beta} a_{\beta\delta} = a_{\alpha\gamma}^{-1} a_{\delta\beta} d_{\beta\gamma} + d_{\alpha\delta}. \quad (1.3.22)$$

Letting $\delta = \alpha$, we see that (1.3.20) is satisfied, so that it is sufficient to have only (1.3.21). If we rearrange (1.3.21) to solve for $K_{\alpha\beta}$ and consider (1.3.17), we obtain

$$K_{\alpha\beta} = d_{\alpha\gamma} \langle B_\gamma B_\beta \rangle + d_{\beta\gamma} \langle B_\gamma B_\alpha \rangle. \quad (1.3.23)$$

This relation is the general linear (i.e. two-subscript) Markov FDR. Its other (equivalent) form is given by (4.1.12) or (4.2.14a). The preceding consideration also confirms the Gaussian form (1.3.16) of the stationary distribution.

Of course, the application of FDR (1.3.23) must confirm (1.3.14). In fact, if we let $B = v$ and compare (1.3.16) with the Maxwell distribution $w(v) = \text{const} \cdot \exp(-mv^2/2kT)$, we have the following matrices:

$$a_{\alpha\gamma} = \frac{m}{kT} \delta_{\alpha\gamma}, \quad \langle v_\alpha v_\gamma \rangle = a_{\alpha\gamma}^{-1} = \frac{kT}{m} \delta_{\alpha\gamma}. \quad (1.3.24)$$

Further, making allowance for the form of the first term on the right-hand side of

(1.3.8), we get $d_{11} = -\beta/m$ and more generally

$$d_{\alpha\gamma} = -\frac{\beta}{m} \delta_{\alpha\gamma}. \quad (1.3.25)$$

Consequently, according to (1.3.23) we obtain

$$K_{\alpha\gamma} = \frac{2kT\beta}{m^2} \delta_{\alpha\gamma}, \quad (1.3.26)$$

i.e. (1.3.14) is valid for the scalar coefficient K , which is defined by the equation $K_{\alpha\beta} = (K/m^2)\delta_{\alpha\beta}$.

We must assume $U(x) = \kappa x^2/2$ in (1.3.5) to derive Einstein's relation from (1.3.23). Then we arrive at

$$a_{11} = \frac{\kappa}{kT}, \quad \langle x^2 \rangle = \frac{kT}{\kappa}. \quad (1.3.27)$$

We get $d_{11} = \mu\kappa$ from the form of the first term of the right-hand side of (1.3.6). Using (1.3.23), we find at $B_1 = x$ that

$$K_{11} = 2kT\mu. \quad (1.3.28)$$

This coincides with (1.3.4) since $D = K_{11}/2$, which is seen from the form of the second term in (1.3.6).

1.3.4 Onsager's Reciprocal Relations

In 1931 *Onsager* [1.13] derived the celebrated reciprocal relations, which form the essential part of linear nonequilibrium thermodynamics. His theory is based on the following assumptions.

1. Only the linear relaxation equations,

$$\dot{A}_\alpha = -d_{\alpha\beta} A_\beta, \quad (1.3.29)$$

are considered, where $A_\alpha = \langle B_\alpha \rangle$ are nonequilibrium averages.

2. The time evolution of the moments $\langle B_\alpha(t)B_\beta(0) \rangle$ is assumed to be ruled by the same law as the relaxation of averages $A_\alpha(t)$ which are described by (1.3.29).

3. The condition of time reversibility of microscopic processes is fulfilled; this is due to the invariance of microscopic equations under time inversion $t \rightarrow -t$. Thus, for the first time the principle of time reversal invariance played an important role in statistical physics.

Naturally, the first assumption is the most important restriction of Onsager's theory. Unfortunately, one cannot establish similar relations beyond the framework of linear thermodynamics. In the second assumption, which demands the same time evolution of the moment $\langle B_\alpha(t)\beta_\beta(0) \rangle$ and of average values $A_\alpha(t) = \langle B_\alpha(t) \rangle$, one implicitly supposes a δ -correlation of Langevin's forces $\xi_\alpha(t)$ in the stochastic equation

$$\dot{B}_\alpha(t) = -d_{\alpha\beta} B_\beta(t) + \xi_\alpha(t). \quad (1.3.30)$$

The second assumption cannot be fulfilled without δ -correlated random forces. A process $\{B_\alpha(t)\}$ becomes a Markov process due to this δ -correlation, which is described by the Fokker–Planck equation (1.3.15). Thus, Onsager’s relation is essentially a linear relation of the Markov theory. Other authors later obtained various non-Markov reciprocal relations. Onsager’s reciprocal relation can be written as

$$L_{\alpha\beta} = L_{\beta\alpha}, \quad (1.3.31)$$

where

$$L_{\alpha\beta} = d_{\alpha\gamma} \langle B_\gamma(t) B_\beta(t) \rangle. \quad (1.3.32)$$

The form of Onsager’s matrix (1.3.32) is analogous to that which is used in (1.3.23) and is not the only possible one. If we use the notation of (1.3.32), equation (1.3.23) takes the form $K_{\alpha\beta} = L_{\alpha\beta} + L_{\beta\alpha}$. Another forms of Onsager’s relation will be given later [see (3.3.5, 4.1.14)].

However, it should be noted that simple Onsager’s relations (1.3.31) are valid only when all B_1, B_2, \dots have the same time parity, i.e. either all of them do not change the sign under time reversal (for example, spatial coordinates x, y, z or charges), or all of them reverse sign (for example, velocities and currents). If there are time-even and time-odd variables, then one has the more complex Onsager–Casimir relations [1.14],

$$L_{\alpha\beta} = \varepsilon_\alpha \varepsilon_\beta L_{\beta\alpha}, \quad (1.3.33)$$

which were obtained in 1945. Here $\varepsilon_\alpha = \pm 1$, where ε_α are defined from the conditions $B_\alpha \rightarrow \varepsilon_\alpha B_\alpha$ for $t \rightarrow -t$. The relation

$$\sigma_{ij} = \sigma_{ji}, \quad (1.3.34)$$

which expresses the symmetry of conductivity tensor σ_{ij} of an anisotropic medium, can be regarded as an example of Onsager’s relation. This tensor is defined by

$$j_i = \sigma_{ik} E_k, \quad \text{i.e. } \mathbf{j} = \boldsymbol{\sigma} \cdot \mathbf{E}, \quad (1.3.35)$$

where \mathbf{E} is the electric field and \mathbf{j} is the electric current density.

The field character of this system should be taken into account for proving (1.3.34) with the help of Onsager’s relations. The density of electric charge $\rho(\mathbf{r})$ is taken as A_α , i.e. the subscript α has the meaning of the radius vector \mathbf{r} . The following charge conservation equation

$$\dot{\rho}(\mathbf{r}_1) = -\nabla_{1\alpha} j_\alpha(\mathbf{r}_1) = -\nabla_{1\alpha} \sigma_{\alpha\beta} E_\beta(\mathbf{r}_1) \quad (1.3.36)$$

[(1.3.35) is used; $\nabla_1 = \partial/\partial r_1$] is taken as (1.3.29). The medium is supposed to be homogeneous, so that $\sigma_{\alpha\beta}$ is independent of \mathbf{r}_1 . According to (1.3.29), the right-hand side of (1.3.36) is supposed to be expressed in terms of $\rho(\mathbf{r}_2)$. Because of the linearity of the problem we can write

$$E_\beta(\mathbf{r}_1) = \int \frac{\delta E_\beta(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)} \rho(\mathbf{r}_2) d\mathbf{r}_2. \quad (1.3.37)$$

Substituting this equation into (1.3.36), we find the matrix $d_{\alpha\beta} = d(\mathbf{r}_1, \mathbf{r}_2)$:

$$d(\mathbf{r}_1, \mathbf{r}_2) = \nabla_{1\alpha} \sigma_{\alpha\beta} \frac{\delta E_\beta(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)}. \quad (1.3.38)$$

Using (1.3.32), we obtain the Onsager matrix

$$\begin{aligned} L(\mathbf{r}_1, \mathbf{r}_2) &= \nabla_{1\alpha} \sigma_{\alpha\beta} \int d\mathbf{r}_3 \frac{\delta E_\beta(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_3)} \langle \rho(\mathbf{r}_3) \rho(\mathbf{r}_2) \rangle \\ &= \nabla_{1\alpha} \sigma_{\alpha\beta} \langle E_\beta(\mathbf{r}_1) \rho(\mathbf{r}_2) \rangle. \end{aligned} \quad (1.3.39)$$

According to Maxwell's equation $\rho = \epsilon \nabla \cdot \mathbf{E}$, the last equation can therefore be written as

$$L(\mathbf{r}_1, \mathbf{r}_2) = \epsilon \nabla_{1\alpha} \nabla_{2\gamma} \sigma_{\alpha\beta} \langle E_\beta(\mathbf{r}_1) E_\gamma(\mathbf{r}_2) \rangle. \quad (1.3.40)$$

The one-time equilibrium correlator of electric field can be found by using the Boltzmann distribution

$$w[E(r)] = \text{const} \cdot \exp \left[-\frac{\epsilon}{2kT} \int E^2(r) dr \right], \quad (1.3.41)$$

where (as is well known from the theory of electricity) $(\epsilon/2) \int E^2(r) dr$ is the full energy of the field E and, consequently, the energy of interacting charges. Applying a formula of the type (1.3.17), we obtain from (1.3.41)

$$\langle E_\beta(\mathbf{r}_1) E_\gamma(\mathbf{r}_2) \rangle = \frac{kT}{\epsilon} \delta_{\alpha\beta} \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (1.3.42)$$

and, therefore, (1.3.40) gives

$$L(\mathbf{r}_1, \mathbf{r}_2) = kT \sigma_{\alpha\beta} \nabla_{1\alpha} \nabla_{2\beta} \delta(\mathbf{r}_{12}). \quad (1.3.43)$$

Using this equation, we immediately obtain $\sigma_{\alpha\beta} = \sigma_{\beta\alpha}$ from Onsager's relations $L(\mathbf{r}_1, \mathbf{r}_2) = L(\mathbf{r}_2, \mathbf{r}_1)$. The method used here and the method applied by Onsager are not identical. Further examples of applications of Onsager's relations will be given later (Sect. 4.4).

1.3.5 Nyquist's Formula

In 1928 Nyquist [1.15] derived for the first time the non-Markov FDR, which is called Nyquist's formula. It was intended for calculating the spectral densities and correlation functions of the thermal noise in linear electrical circuits. Only afterwards was it realized that the formula could be applied for calculation of the thermal noise in systems of other nature too, for example, in linear mechanical systems.

By applying Nyquist's formula one finds the spectral density of a random electromotive force (e.m.f.) (a mechanical force in mechanical systems) arising in dissipative elements of the circuits. The general one-component formula has the form

$$S_\varepsilon(\omega) = 2kT \operatorname{Re}\{Z(\omega)\}, \quad (1.3.44)$$

where $Z(\omega)$ is the total impedance of a two-terminal impedor. The impedance determines the current $I(\omega) = Z^{-1}(\omega)u(\omega)$ (Fig. 1.1) appearing due to an external e.m.f. $u(\omega)$. The spectral density of the random force $\mathcal{E}(t)$ is defined by

$$S_{\mathcal{E}}(\omega) = \int \exp(-i\omega t_{12}) \langle \mathcal{E}(t_1)\mathcal{E}(t_2) \rangle dt_2, \quad t_{12} = t_1 - t_2. \quad (1.3.45)$$

In the many-component case formula (5.6.41), which will be derived later, replaces (1.3.44).

Applying (1.3.44) and the equation $I(\omega) = \mathcal{E}(\omega)/Z(\omega)$, we can easily find the spectral density of current in the case of the short-circuited two-terminal impedor:

$$S_I(\omega) = 2kT|Z(\omega)|^{-2} \operatorname{Re}\{Z(\omega)\} = 2kT \operatorname{Re}\{Y(\omega)\}, \quad Y(\omega) = 1/Z(\omega). \quad (1.3.46)$$

1. Let us now suppose that the two-terminal impedor consists of two complex resistors with resistances $Z_1(\omega)$ and $Z_2(\omega)$ connected in series, so that $Z(\omega) = Z_1(\omega) + Z_2(\omega)$. Let us find the spectral density of the voltage

$$V = \mathcal{E}_1 - Z_1 I = Z_2 I - \mathcal{E}_2 \quad (1.3.47)$$

across the resistor $Z_1(\omega)$ or $Z_2(\omega)$ (Fig. 1.2). Here \mathcal{E}_i is the random e.m.f. arising in the resistor $Z_i(\omega)$. Substituting $I = (\mathcal{E}_1 + \mathcal{E}_2)/(Z_1 + Z_2)$, we obtain

$$V = (Z_2 \mathcal{E}_1 - Z_1 \mathcal{E}_2)/(Z_1 + Z_2). \quad (1.3.48)$$

For random e.m.f.'s \mathcal{E}_1 and \mathcal{E}_2 arising in resistors $Z_1(\omega)$ and $Z_2(\omega)$ formula of the type (1.3.44) – $S_{\mathcal{E}_i}(\omega) = kT \operatorname{Re}\{Z_i(\omega)\}$ – is valid.

Using these formulas, we obtain from (1.3.48)

$$S_V(\omega) = 2kT|Z_1 + Z_2|^{-2}(|Z_2|^2 \operatorname{Re}\{Z_1\} + |Z_1|^2 \operatorname{Re}\{Z_2\}). \quad (1.3.49)$$

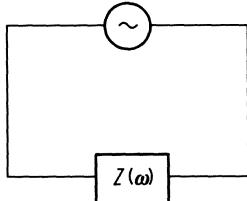


Fig. 1.1. Impedor with impedance $Z(\omega)$ to which an arbitrary varying voltage is applied

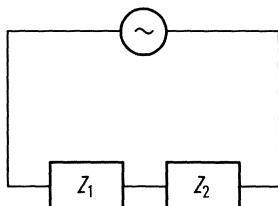


Fig. 1.2. Two impedors connected in series

If, in particular, we make $|Z_2|$ approach infinity and if we replace $Z_1(\omega)$ by $Z(\omega)$, then we find that the spectral density of the potential difference across the terminals of the open two-terminal impedor is also defined by (1.3.44). This can be used for the shorter derivation of (1.3.49). In fact, if the two-terminal impedor is made by connecting $Z_1(\omega)$ and $Z_2(\omega)$ in parallel, its impedance is $Z = Z_1 Z_2 / (Z_1 + Z_2)$. But this complex two-terminal impedor is open (Fig. 1.2). Consequently, the fluctuations of the potential difference V across the impedor can be defined by substituting $Z = Z_1 Z_2 / (Z_1 + Z_2)$ into (1.3.44):

$$S_V(\omega) = 2kT \operatorname{Re}\{Z_1 Z_2 / (Z_1 + Z_2)\} . \quad (1.3.50)$$

We can easily verify that this result is equivalent to (1.3.49). Thus, Nyquist's formula has the necessary properties of self-consistency.

2. Let us apply Nyquist's formula to the Brownian particle motion that has been described by (1.3.8). By introducing the external force F_1 acting along the x -axis, we get

$$m \frac{dv}{dt} + \mu^{-1} v = F_1 + F_2 . \quad (1.3.51)$$

The fluctuational force F_2 drops out by averaging, and we arrive at

$$(i\omega m + \mu^{-1}) \langle v \rangle = F_1 . \quad (1.3.52)$$

But by analogy with the case of electrical circuit, equation $Z(\omega)v = F_1$ must hold; here v and F_1 have been taken instead of I and u . Consequently, we have

$$Z(\omega) = i\omega m + \mu^{-1} . \quad (1.3.53)$$

According to Nyquist's formula (1.3.44), we can now find the spectral density of the random force F_2 :

$$S_2(\omega) = 2kT\mu^{-1} . \quad (1.3.54)$$

This means that the correlation function of the random (Langevin) force is

$$\langle F_2(t_1)F_2(t_2) \rangle = 2kT\mu^{-1} \delta(t_{12}) . \quad (1.3.55)$$

Of course, this formula is in accordance with (1.3.10, 14). Using (1.3.44) and equation (1.3.51) at $F_1 = 0$, we find the expression for the velocity spectral density:

$$S_v(\omega) = 2kT\mu^{-1}|Z(\omega)|^{-2} = \frac{2kT}{\omega^2 m^2 \mu^2 + 1} . \quad (1.3.56a)$$

The correlation function

$$\langle v(t_1)v(t_2) \rangle = kTm^{-1} \exp(-t_{12}/m\mu) \quad (1.3.56b)$$

corresponds to this spectral density.

3. Let us now return to the diffusion coefficient D entering into (1.3.1). Since

$$x(t) - x_0 = \int_0^t v(t') dt' , \quad (1.3.57)$$

(1.3.1) can be written as

$$\int_0^t \int_0^t \langle v(t_1)v(t_2) \rangle dt_1 dt_2 = 2Dt . \quad (1.3.58)$$

Differentiating both sides of this equation with respect to t gives

$$D = \int_0^t \langle v(t)v(t') \rangle dt' . \quad (1.3.59)$$

The diffusion coefficient D is assumed to be independent of t . In order that this independence be valid the time t must be sufficiently large in (1.3.1, 58, 59); it must be much more than the correlation time of the velocity $v(t)$, i.e. the time $m\mu$ [see (1.3.56b)]. But if the time t is so large, then in (1.3.59) the integration interval may be set equal to infinity. Consequently, we obtain the following expression for time-independent diffusion coefficient:

$$D = \int_0^\infty \langle v(t)v(t') \rangle dt' \quad (1.3.60)$$

or

$$2D = \int_{-\infty}^\infty \langle v(t_1)v(t_2) \rangle dt_{12} \quad (1.3.61)$$

if the stationarity of fluctuation and the symmetry of the correlation function $\langle v(0)v(\tau) \rangle = \langle v(0)v(-\tau) \rangle$ are used.

Taking into account the definition of the velocity spectral density

$$S_v(\omega) = \int \exp(i\omega t_{21}) \langle v(t_1)v(t_2) \rangle dt_{21} , \quad (1.3.62)$$

one can easily see that (1.3.61) can be written as

$$2D = S_v(0) . \quad (1.3.63)$$

Formulas (1.3.61, 63) are valid for any form of correlation function and velocity spectral density (only the conditions of stationarity and of correlation function vanishing at large t_{12} are important).

Using (1.3.63) in the particular case (1.3.56a) we find $D = kT\mu$, i.e. we again obtain Einstein's formula (1.3.4).

1.3.6 The Callen–Welton FDT and Kubo's Formula

In 1951 *Callen* and *Welton* [1.16] proved the so-called fluctuation–dissipation theorem (FDT). This theorem is the quantum version of the linear non-Markov FDR. In the non-quantum limit it is equivalent to Nyquist's formula. The following results of Callen and Welton should be regarded as great achievements:

1. The generalization of the theory to the quantum case.
2. The universal formulation appropriate to internal parameters B_α and forces $h_\alpha(t)$ of any nature. The forces conjugate to B_α are defined by the form of the

interaction Hamiltonian

$$\mathcal{H}_{\text{int}} = - \sum_{\alpha} B_{\alpha} h_{\alpha}. \quad (1.3.64)$$

Furthermore, general response functions or admittances $G_{\alpha, \beta}$ are introduced by

$$\langle B(t_1) \rangle = \int G(t_1 - t_2) h(t_2) dt_2 \quad (1.3.65)$$

(for simplicity the one-parameter case is taken).

3. The universal quantum-mechanical proof is also an achievement of these authors.

In the one-component case the Callen–Welton relation has the form

$$S_B(\omega) = - \hbar \coth \frac{\hbar \omega}{2kT} \text{Im}\{G(\omega)\}, \quad (1.3.66)$$

where

$$G(\omega) = \int \exp(-i\omega t_{12}) G(t_{12}) dt_{12}, \quad (1.3.67)$$

and $S_B(\omega)$ is the spectral density of the process $B(t)$. In the more general case the Callen–Welton relation is given by (5.3.9).

Let us show the connection between (1.3.66) and the Nyquist formula. Differentiating both sides of (1.3.65) with respect to t gives

$$\langle I(t_1) \rangle = \int Y(t_1 - t_2) h(t_2) dt_2, \quad (1.3.68)$$

where

$$I(t_1) = \frac{dB(t_1)}{dt_1}, \quad Y(t_{12}) = \frac{dG(t_{12})}{dt_{12}}. \quad (1.3.69)$$

Introducing $Y(\omega)$ by the formula

$$Y(\omega) = \int \exp(-i\omega t_{12}) Y(t_{12}) dt_{12}, \quad (1.3.70)$$

which is analogous to (1.3.67), we have $Y(\omega) = i\omega G(\omega)$. Consequently,

$$\text{Im}\{G(\omega)\} = \omega^{-1} \text{Im}\{Y(\omega)/i\} = -\omega^{-1} \text{Re}\{Y(\omega)\}. \quad (1.3.71)$$

Considering (1.3.71) and the formula $S_I(\omega) = \omega^2 S_B(\omega)$, which follows from the equation $I = dB/dt$, we transform (1.3.66) to the form

$$S_I(\omega) = \hbar \omega \coth \left(\frac{\hbar \omega}{2kT} \right) \text{Re}\{Y(\omega)\}. \quad (1.3.72)$$

This equation represents the direct quantum generalization of formula (1.3.46), which is equivalent to Nyquist's formula. Hence, we see that in the quantum case the multiplier $(\hbar\omega/2kT) \coth(\hbar\omega/2kT)$ must be substituted into Nyquist's formula (1.3.44).

The Callen–Welton FDT has a great many applications. Kubo's formula is one of the consequences of FDT. It has the form

$$G(t) = \int_0^\beta d\lambda \langle \dot{B}(-i\hbar\lambda)B(t) \rangle \quad (1.3.73)$$

for $t > 0$ ($\beta^{-1} = kT$). It was independently derived by *Kubo* [1.17] in 1957.

Formula (1.3.73) represents the quantum generalization of the nonquantum formula

$$G(t) = \beta \langle \dot{B}(0)B(t) \rangle \quad (1.3.74)$$

for $t > 0$. Comparing (1.3.73) and (1.3.74), we see that the transition from the nonquantum case to the quantum one consists in the replacement of the moment $\langle \dot{B}(0)B(t) \rangle$ by the specific “moment”

$$\frac{1}{\beta} \int_0^\beta d\lambda \langle \dot{B}(-i\hbar\lambda)B(t) \rangle .$$

This also applies to other moments. This sort of replacement may be also done in formula (1.3.61) in order to obtain the quantum generalization of this formula. It takes the form

$$2D = \frac{1}{\beta} \int_{-\infty}^{\infty} dt_{21} \int_0^\beta d\lambda \langle v(t_1 - i\hbar\lambda)v(t_2) \rangle . \quad (1.3.75)$$

Other transport coefficients can be written in an analogous form.

In conclusion, we note that Nyquist's formula (1.3.44) also keeps its value in the quantum case when $S_\mathcal{E}(\omega)$ is assumed to be the Fourier transform of the correlator

$$\beta^{-1} \int_0^\beta d\lambda \langle \mathcal{E}(t_1 - i\hbar\lambda)\mathcal{E}(t_2) \rangle .$$

1.3.7 Mori's Relation

Returning to the Brownian motion theory in the nonquantum case, we now suppose that the medium in which Brownian particles are moving is such that the frictional force F_1 along the x -axis depends inertially on the velocity:

$$F_1(t_1) = -m \int f(t_1 - t_2)v(t_2) dt_2 , \quad (1.3.76)$$

where $f(\tau)$ is an influence function. Then the equation of motion has the form

$$\dot{v}(t_1) = - \int f(t_1 - t_2)v(t_2) dt_2 + \xi(t_1) , \quad (1.3.77)$$

where

$$\xi(t) = \frac{F_2(t)}{m} . \quad (1.3.78)$$

In 1965 Mori [1.18] obtained a relation that allowed one to find the correlation function of the random force $\xi(t)$ in such equations. In the present case this relation has the form

$$\langle \xi(t_1)\xi(t_2) \rangle = \langle v^2(0) \rangle f(t_1 - t_2) \quad \text{at} \quad t_1 > t_2. \quad (1.3.79)$$

On the one hand, this relation is not a great achievement since the random force correlator in (1.3.77) may be determined by means of Nyquist's formula; but on the other hand, Mori's result is of interest since it was obtained by the general method of Liouville's equation and projection operator in phase space (Sect. 4.2, Vol. 2).

Let us use (1.3.79) for calculating the spectral density of the velocity $v_x(t)$. Considering that $m\langle v_x^2(0) \rangle = kT$, we can obtain from (1.3.79) the total correlator

$$\langle \xi(t_1)\xi(t_2) \rangle = \frac{kT}{m} [f(t_1 - t_2) + f(t_2 - t_1)] \quad (1.3.80)$$

(the difference $t_1 - t_2$ is arbitrary). We have supposed that $f(\tau) = 0$ for $\tau < 0$. Performing the Fourier transformation and denoting it by

$$F(\omega) = \int \exp(-i\omega t_{12}) f(t_{12}) dt_{12}, \quad (1.3.81)$$

we obtain from (1.3.80)

$$S_\xi(\omega) = 2kTm^{-1} \operatorname{Re}\{F(\omega)\}. \quad (1.3.82)$$

Taking into consideration that (1.3.77) has the spectral form $[i\omega + F(\omega)]v\{\omega\} = \xi(\omega)$ and using (1.3.82), we find

$$S_v(\omega) = \frac{2kTm^{-1} \operatorname{Re}\{F(\omega)\}}{\omega^2 + |F(\omega)|^2}. \quad (1.3.83)$$

Thus, the desired spectral density has been found. Using this, we easily find, in particular, the diffusion coefficient of the Brownian particles. According to (1.3.63), we have

$$D = \frac{kT}{mF(0)}. \quad (1.3.84)$$

1.3.8 Thermal Noise of Nonlinear Resistance: The Markov Theory

Let us proceed to consider the problems related to nonlinear FDRs. We consider a circuit (Fig. 1.3) consisting of an inductor with inductance L , a nonlinear resistance and a power supply with constant e.m.f. and zero internal resistance. Let us suppose that the nonlinear resistance has quadratic nonlinearity and that for not very large values of I its voltage-current characteristic may be written in the form

$$V = RI + \frac{1}{2}\alpha I^2. \quad (1.3.85)$$

Denoting the e.m.f. of the power supply by u and using (1.3.85), we can easily write

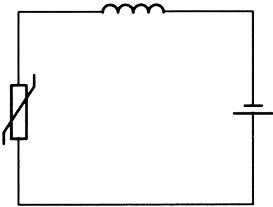


Fig. 1.3. Electric circuit with a nonlinear resistor, an inductor and a voltage source

the equation describing this circuit if we neglect fluctuations:

$$L \frac{dI}{dt} + RI + \frac{1}{2} \alpha I^2 = u . \quad (1.3.86)$$

Because of nonlinearity, in the presence of the constant external e.m.f. u and the constant average current induced by it in the circuit, we must use a quadratic FDR rather than Nyquist's formula or linear FDT for determination of the spectral density of the fluctuational current or for determination of the corresponding correlation function. The intensity of fluctuational e.m.f. in this circuit was calculated [1.6] by using the Markov quadratic FDR in 1970. Let us describe this FDR. If the probability density of a parameter B satisfies the equation

$$\begin{aligned} \dot{w}(B) = & - \frac{\partial}{\partial B_\alpha} [K_\alpha(B)w] + \frac{1}{2} \frac{\partial^2}{\partial B_\alpha \partial B_\beta} [K_{\alpha\beta}(B)w] \\ & - \frac{1}{6} \frac{\partial^3}{\partial B_\alpha \partial B_\beta \partial B_\gamma} [K_{\alpha\beta\gamma}w] + \dots , \end{aligned} \quad (1.3.87)$$

which corresponds to the Markov process $B(t)$, one of the two quadratic Markov FDRs has the form

$$\begin{aligned} K_{\alpha\beta,\delta} \langle B_\delta B_\gamma \rangle = & - K_{\alpha,\rho\sigma} \langle B_\rho B_\beta \rangle \langle B_\sigma B_\gamma \rangle - K_{\alpha,\rho} \langle B_\rho B_\beta B_\gamma \rangle \\ & - K_{\beta,\rho\sigma} \langle B_\rho B_\alpha \rangle \langle B_\sigma B_\gamma \rangle - K_{\beta,\rho} \langle B_\rho B_\alpha B_\gamma \rangle \\ & + \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma [K_{\gamma,\rho\sigma} \langle B_\rho B_\alpha \rangle \langle B_\sigma B_\beta \rangle + K_{\gamma,\rho} \langle B_\rho B_\alpha B_\beta \rangle] , \end{aligned} \quad (1.3.88)$$

where

$$K_{\alpha,\rho\dots\omega} = \frac{\partial K_\alpha(B)}{\partial B_\rho \dots \partial B_\omega} , \quad K_{\alpha\beta,\delta} = \frac{\partial K_{\alpha\beta}(B)}{\partial B_\delta} \quad (1.3.89)$$

(the derivatives are taken at the points $B = \langle B \rangle$); the moments are the one-time central monents, i.e. they correspond to $\langle B \rangle = 0$; ε_α have the same sense as in (1.3.33).

Another form of writing the last FDR is given by (4.1.16). For time-even parameters ($\varepsilon_\alpha = 1$) the FDR (1.3.88) was obtained in [1.4], and for arbitrary parameters it was obtained in [1.5].

We now apply (1.3.88) to the above-mentioned problem. The current I is taken as B_1 , then $\varepsilon_1 = -1$. Because of the inductance linearity the triple moment in

(1.3.88) vanishes and the double one is equal to $\langle B_1^2 \rangle = \langle I^2 \rangle = kT/L$. Therefore, the relation (1.3.88) takes the form

$$K_{11,1} = -3kTL^{-1}K_{1,11}. \quad (1.3.90)$$

From equation (1.3.86) we have $dI/dt = -(RI + \frac{1}{2}\alpha I^2)/L$ at $u = 0$. In the presence of fluctuations the average current derivative is defined by similar expression

$$\frac{d\langle I \rangle}{dt} = K_1(I) = -\frac{R}{L}I - \frac{\alpha}{2L}I^2. \quad (1.3.91)$$

Here we use the fact that $K_1(B)$ is nothing but the average derivative $\langle \dot{B}_\alpha \rangle$ expressed in terms of B . By differentiating we obtain $K_{11,1} = -\alpha/L$ from (1.3.91). Consequently, formula (1.3.90) gives

$$K_{11,1} = 3kT\alpha L^{-2}. \quad (1.3.92)$$

Considering the relation $K_{11}(0) = 2kTR/L^2$ obtained by means of the linear FDR (1.3.23), we get

$$K_{11}(I) = K_{11}(0) + K_{11,1}I = kTL^{-2}(2R + 3\alpha I). \quad (1.3.93)$$

Thus, in equation (1.3.87), which is applied to the problem under study, we know completely not only the term with the first derivative, but also the term with the second derivative. Now we can take the external e.m.f. into consideration. If the current it induces considerably exceeds the fluctuational current component, we can take $\langle I \rangle$ instead of I in (1.3.93). Then we obtain

$$w(I) = L^{-1} \frac{\partial}{\partial I} \left(RI + \frac{\alpha}{2} I^2 - u \right) w + \frac{1}{2} kTL^{-2}(2R + 3\alpha\langle I \rangle) \frac{\partial^2 w}{\partial I^2}. \quad (1.3.94)$$

The terms with higher derivatives are omitted. The stochastic equation

$$L \frac{\partial I}{\partial t} = u - RI - \frac{\alpha}{2} I^2 + (kT)^{1/2}(2R + 3\alpha\langle I \rangle)^{1/2} \zeta(t) \quad (1.3.95)$$

corresponds to (1.3.94), where $\zeta(t)$ is the random process with zero mean value and unit spectral density $S_\zeta(\omega) = 1$. Since $(kT)^{1/2}$ entering into (1.3.95) is small, the small fluctuations of current occur around the mean value $\langle I \rangle$ determined from equation $R\langle I \rangle + 2^{-1}\alpha\langle I \rangle^2 = u$. From (1.3.95) we readily obtain the linearized equation for deriving $\delta I = I - \langle I \rangle$:

$$L \frac{d\delta I}{dt} = (R + \alpha\langle I \rangle)\delta I + (kT)^{1/2}(2R + 3\alpha\langle I \rangle)^{1/2} \zeta(t). \quad (1.3.96)$$

Proceeding to the spectra $I(\omega)$, $\zeta(\omega)$, we easily solve the last equation and find the spectral density of the current fluctuations:

$$S_I(\omega) = \frac{kT(2R + 3\alpha\langle I \rangle)}{L^2\omega^2 + (R + \alpha\langle I \rangle)^2}. \quad (1.3.97)$$

Strictly, this result is valid only in the framework of the voltage–current characteristic approximation (1.3.85).

In 1970, the second Markov FDR (4.1.18) was also established [1.5, 6]; it helps, for instance, to calculate the triple moment $\langle I(t_1)I(t_2)I(t_3) \rangle$ or $\langle I(\omega_1)I(\omega_2)I(\omega_3) \rangle$ in the above example.

1.3.9 Thermal Noise of Nonlinear Resistance: The Non-Markov Theory

Let the inductor in the circuit in Fig. 1.3 be replaced by an arbitrary linear two-terminal impedor with impedance $Z_0(\omega)$ (Fig. 1.4). In order to write the equation for the circuit obtained, in (1.3.86) let us proceed to the spectra

$$\begin{aligned} I(\omega) &= (2\pi)^{-1/2} \int e^{-i\omega t} I(t) dt, \\ u(\omega) &= (2\pi)^{-1/2} \int e^{-i\omega t} u(t) dt. \end{aligned} \quad (1.3.98)$$

We have

$$(i\omega L + R)I(\omega) + \frac{1}{2}(2\pi)^{-1/2}\alpha \int \delta(\omega - \omega' - \omega'')I(\omega')I(\omega'')d\omega' d\omega'' = u(\omega). \quad (1.3.99)$$

Now we replace $i\omega L$ by $Z_0(\omega)$:

$$u(\omega) = [Z_0(\omega) + R]I(\omega) + \frac{1}{2}(2\pi)^{-1/2}\alpha \int \delta(\omega - \omega' - \omega'')I(\omega')I(\omega'')d\omega' d\omega''. \quad (1.3.100)$$

After this replacement the current $I(t)$ becomes, generally speaking, the non-Markov process, arbitrary $Z_0(\omega)$. Therefore, the non-Markov FDR must be used for determining the spectral density of fluctuational current.

Let us solve (1.3.100) and find $I(\omega)$. We get

$$\begin{aligned} I(\omega) &= [Z_0(\omega) + R]^{-1} \left[u(\omega) - \frac{1}{2}(2\pi)^{-1/2}\alpha \right. \\ &\quad \times \left. \int \delta(\omega - \omega' - \omega'')I(\omega')I(\omega'')d\omega' d\omega'' \right]. \end{aligned} \quad (1.3.101)$$

Allowing the error to be of order α^2 , we can substitute the less precise expression

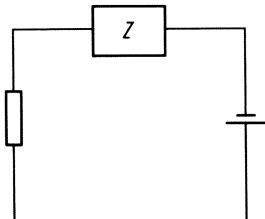


Fig. 1.4. The circuit of Fig. 1.3 in which the inductor is replaced by an arbitrary linear impedor

$I(\omega) = [Z_0(\omega) + R]^{-1} u(\omega)$ into the right-hand side of the last equation. This gives

$$\begin{aligned} I(\omega) &= Y(\omega)u(\omega) - \frac{1}{2}(2\pi)^{-1/2}\alpha Y(\omega) \\ &\times \int \delta(\omega - \omega' - \omega'') Y(\omega') Y(\omega'') u(\omega') u(\omega'') d\omega' d\omega'' , \end{aligned} \quad (1.3.102)$$

where $Y(\omega) = Z^{-1}(\omega) = [Z_0(\omega) + R]^{-1}$. Formula (1.3.102) may be reduced to the form

$$\begin{aligned} I(\omega) &= Y(\omega)u(\omega) - \frac{1}{2}(2\pi)^{-1/2}\alpha Y(\omega) \\ &\times \int \delta(\omega + \omega_2 + \omega_3) Y^*(\omega_2) Y^*(\omega_3) u^*(\omega_2) u^*(\omega_3) d\omega_2 d\omega_3 , \end{aligned} \quad (1.3.103)$$

where $\omega_2 = -\omega'$, $\omega_3 = -\omega''$. The quadratic admittance is defined by

$$I(\omega_1) = Y(\omega_1)u(\omega_1) + \frac{1}{2} \int Y(\omega_1; \omega_2, \omega_3) u^*(\omega_2) u^*(\omega_3) d\omega_2 d\omega_3 . \quad (1.3.104)$$

Comparing equation (1.3.104) with (1.3.103), we find the form of the admittance in the case under study:

$$Y(\omega_1; \omega_2, \omega_3) = -(2\pi)^{-1/2}\alpha Y(\omega_1) Y^*(\omega_2) Y^*(\omega_3) \delta(\omega_1 + \omega_2 + \omega_3) . \quad (1.3.105)$$

One of the non-Markov FDRs determines the derivative $\delta \langle I(\omega_1) I(\omega_2) \rangle / \delta u^*(\omega_3)$, and has the form

$$\frac{\delta \langle I(\omega_1) I(\omega_2) \rangle}{\delta u^*(\omega_3)} = kT [Y(\omega_1; \omega_2, \omega_3) + Y(\omega_2; \omega_1, \omega_3) - Y^*(\omega_3; \omega_1, \omega_2)] \quad (1.3.106)$$

[see (5.3.99)]. This equation is nothing but the one-component nonquantum version of one of the two quadratic FDRs derived by Efremov [1.7].

Using (1.3.106) and the relation $\langle I(\omega_1) I(\omega_2) \rangle_0 = 2kT \operatorname{Re}\{Y(\omega_1)\} \delta(\omega_1 + \omega_2)$, which is equivalent to the nonquantum linear FDT, we can find the correlator of current:

$$\begin{aligned} \langle I(\omega_1) I(\omega_2) \rangle &= 2kT \operatorname{Re}\{Y(\omega_1)\} \delta(\omega_1 + \omega_2) \\ &+ kT \int [Y(\omega_1; \omega_2, \omega_3) + Y(\omega_2; \omega_1, \omega_3) \\ &- Y^*(\omega_3; \omega_1, \omega_2)] u^*(\omega_3) d\omega_3 . \end{aligned} \quad (1.3.107)$$

This formula is valid in the presence of an external e.m.f. $u(t)$. If this e.m.f. is constant, then $u(\omega) = (2\pi)^{1/2} u \delta(\omega)$ and the last formula gives

$$\begin{aligned} \langle I(\omega_1) I(\omega_2) \rangle &= 2kT \operatorname{Re}\{Y(\omega_1)\} \delta(\omega_1 + \omega_2) \\ &+ (2\pi)^{1/2} kTu [Y(\omega_1; \omega_2, 0) \\ &+ Y(\omega_2; \omega_1, 0) - Y^*(0; \omega_1, \omega_2)] . \end{aligned} \quad (1.3.108)$$

Expression (1.3.105) must be substituted into the last formula. After that we have

$$\langle I(\omega_1)I(\omega_2) \rangle = S_I(\omega_1)\delta(\omega_1 + \omega_2), \quad (1.3.109)$$

where

$$S_I(\omega) = 2kT \operatorname{Re}\{Y(\omega)\} - kT\alpha u Y(0)[2 \operatorname{Re}\{Y^2(\omega)\} - |Y(\omega)|^2]. \quad (1.3.110)$$

Here $Y(\omega) = [Z_0(\omega) + R]^{-1}$, as mentioned earlier.

The second quadratic FDR determines the triple moment. In the nonquantum case it takes the form

$$\langle I(\omega_1)I(\omega_2)I(\omega_3) \rangle = 6(kT)^2 i \{ \operatorname{Im}\{Y(\omega_1; \omega_2, \omega_3)\} \}_{\text{sym}} \quad (1.3.111)$$

[see (5.3.75)]. Here $\{\dots\}_{\text{sym}}$ denotes the operation of symmetrization of the expression in braces with respect to the subscripts 1, 2, 3.

Other examples of the application of FDRs will be considered later.

2. Auxiliary Information Concerning Probability Theory and Equilibrium Thermodynamics

In this chapter we present some facts and concepts of the moment and correlator theory, of the Markov process theory and of equilibrium statistical thermodynamics, which will be useful for subsequent theories. In Sect. 2.2 we emphasize that two different versions of some important formulas of equilibrium statistical thermodynamics are possible. The duality underlines the theory; namely, there exist two different main distributions in phase space: the Gibbs distribution and the microcanonical distribution. Accordingly, the equilibrium probability density of internal parameters can be written in two ways: by using free energy and by using entropy. The duality of some initial formulas of equilibrium thermodynamics leads to two possible versions of nonequilibrium thermodynamics. For convenience, we will regard one of them, namely, the kT -version, as the main version, and the other, i.e. the k -version, as a modified version.

2.1 Moments and Correlators

2.1.1 Moments and the Characteristic Function

Suppose we have random variables ξ_1, \dots, ξ_n (n is arbitrary), which have the joint probability density $w(\xi_1, \dots, \xi_n)$. The mean value

$$\langle \xi_{\alpha_1} \dots \xi_{\alpha_n} \rangle = \int \xi_{\alpha_1} \dots \xi_{\alpha_n} w(\xi_1, \dots, \xi_n) d\xi_1 \dots d\xi_n \quad (2.1.1)$$

is called the moment.

The characteristic function $\Theta(iu_1, \dots, iu_n)$ defined by

$$\begin{aligned} \Theta(iu_1, \dots, iu_n) &= \left\langle \exp\left(\sum_{\alpha=1}^n iu_{\alpha} \xi_{\alpha} \right) \right\rangle \\ &= \int \exp\left(\sum_{\alpha=1}^n iu_{\alpha} \xi_{\alpha} \right) w(\xi_1, \dots, \xi_n) d\xi_1 \dots d\xi_n . \end{aligned} \quad (2.1.2)$$

Using (2.1.1, 2), we easily verify that the moments can be expressed in terms of the characteristic function:

$$\langle \xi_{\alpha_1} \dots \xi_{\alpha_m} \rangle = i^{-m} \left[\frac{\partial^m \Theta(iu_1, \dots, iu_n)}{\partial u_{\alpha_1} \dots \partial u_{\alpha_m}} \right]_{u=0} , \quad m \geq 1 . \quad (2.1.3)$$

Here $u = 0$ means that $u_1 = 0, \dots, u_n = 0$.

If the characteristic function is analytic at the “zero-point”, i.e. at the point where all u 's are equal to zero, the Taylor formula is valid, i.e.

$$\Theta(iu_1, \dots, iu_n) = 1 + \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{\alpha_1, \dots, \alpha_m} \left[\frac{\partial^m \Theta}{\partial u_{\alpha_1} \dots \partial u_{\alpha_m}} \right]_{u=0} u_{\alpha_1} \dots u_{\alpha_m}. \quad (2.1.4)$$

The first term of this expression is equal to unity since $\Theta(0) = 1$, as is seen from (2.1.2). Considering (2.1.3), we thus obtain

$$\Theta(iu_1, \dots, iu_n) = 1 + \sum_{m=1}^{\infty} \frac{i^m}{m!} \sum_{\alpha_1, \dots, \alpha_m} \langle \xi_{\alpha_1} \dots \xi_{\alpha_m} \rangle u_{\alpha_1} \dots u_{\alpha_m}. \quad (2.1.5)$$

Hence, the characteristic function may be expressed in terms of moments. The last formula may be used only when all moments are finite and the expansion on the right-hand side converges.

2.1.2 Correlators and Their Relationship with Moments

The correlator $\langle \xi_{\alpha_1}, \dots, \xi_{\alpha_m} \rangle$ is defined by

$$\langle \xi_{\alpha_1}, \dots, \xi_{\alpha_m} \rangle = i^{-m} \left[\frac{\partial^m \ln \Theta(iu)}{\partial u_{\alpha_1} \dots \partial u_{\alpha_m}} \right]_{u=0}. \quad (2.1.6)$$

Unlike a moment, a correlator has the following property: it is equal to zero if the random variables $\xi_{\alpha_1}, \dots, \xi_{\alpha_m}$ can be divided into at least two groups, so that the variables from one group are statistically independent of the variables from the other group. In fact, if the random variables $\xi_{\alpha_1}, \dots, \xi_{\alpha_k}$ are statistically independent of $\xi_{\alpha_{k+1}}, \dots, \xi_{\alpha_m}$, the probability density and, therefore, the characteristic function is equal to the product of the two functions

$$\begin{aligned} w(\xi_{\alpha_1}, \dots, \xi_{\alpha_m}) &= w_1(\xi_{\alpha_1}, \dots, \xi_{\alpha_k}) w_2(\xi_{\alpha_{k+1}}, \dots, \xi_{\alpha_m}), \\ \Theta(iu_{\alpha_1}, \dots, iu_{\alpha_m}) &= \Theta_1(iu_{\alpha_1}, \dots, iu_{\alpha_k}) \Theta_2(iu_{\alpha_{k+1}}, \dots, iu_{\alpha_m}). \end{aligned} \quad (2.1.7)$$

Consequently,

$$\ln \Theta(v_{\alpha_1}, \dots, v_{\alpha_m}) = \ln \Theta_1(v_{\alpha_1}, \dots, v_{\alpha_k}) + \ln \Theta_2(v_{\alpha_{k+1}}, \dots, v_{\alpha_m}) \quad (2.1.8)$$

($v_{\alpha} = iu_{\alpha}$) and according to equation (2.1.6), which may be written as

$$\langle \xi_{\alpha_1}, \dots, \xi_{\alpha_m} \rangle = \frac{\partial^m \ln \Theta_1(v_{\alpha_1}, \dots, v_{\alpha_k})}{\partial v_{\alpha_1} \dots \partial v_{\alpha_k} \partial v_{\alpha_{k+1}} \dots \partial v_{\alpha_m}} + \frac{\partial^m \Theta_2(v_{\alpha_{k+1}}, \dots, v_{\alpha_m})}{\partial v_{\alpha_1} \dots \partial v_{\alpha_k} \partial v_{\alpha_{k+1}} \dots \partial v_{\alpha_m}}. \quad (2.1.9)$$

We obtain that the correlator $\langle \xi_{\alpha_1}, \dots, \xi_{\alpha_m} \rangle$ is equal to zero. Just as we have obtained (2.1.5) from (2.1.3), from (2.1.6) we now obtain

$$\Theta(v_1, \dots, v_n) = \exp \left\{ \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{\alpha_1, \dots, \alpha_m=1}^n \langle \xi_{\alpha_1}, \dots, \xi_{\alpha_m} \rangle v_{\alpha_1} \dots v_{\alpha_m} \right\}. \quad (2.1.10)$$

We assume that the expansion within the exponent converges. Since formula (2.1.5) has the same left-hand side as (2.1.10), the right-hand sides of these formulas may be equated. Thus, we obviously have

$$\begin{aligned} 1 + \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{\alpha_1, \dots, \alpha_m=1}^n \langle \xi_{\alpha_1} \dots \xi_{\alpha_m} \rangle v_{\alpha_1} \dots v_{\alpha_m} \\ = \exp \left\{ \sum_{k=1}^{\infty} \frac{1}{k!} \sum_{\beta_1, \dots, \beta_k=1}^n \langle \xi_{\beta_1}, \dots, \xi_{\beta_k} \rangle v_{\beta_1} \dots v_{\beta_k} \right\}. \end{aligned} \quad (2.1.11)$$

This equation is called the generating equation because multiple partial differentiation with respect to the components of the vector $v = (v_1, \dots, v_n)$ and equating v to zero give various formulas expressing moments in terms of correlators. By differentiating once with respect to v and equating v to zero, we obtain the coincidence of the moment $\langle \xi_\alpha \rangle$ with the correlator $\langle \xi_\alpha \rangle$. This explains the identical notation of these quantities.

Double differentiation gives

$$\langle \xi_{\alpha_1} \xi_{\alpha_2} \rangle = \langle \xi_{\alpha_1}, \xi_{\alpha_2} \rangle + \langle \xi_{\alpha_1} \rangle \langle \xi_{\alpha_2} \rangle. \quad (2.1.12)$$

Performing triple differentiation and equating v to zero, we have the formula

$$\begin{aligned} \langle \xi_{\alpha_1} \xi_{\alpha_2} \xi_{\alpha_3} \rangle &= \langle \xi_{\alpha_1}, \xi_{\alpha_2}, \xi_{\alpha_3} \rangle + \langle \xi_{\alpha_1}, \xi_{\alpha_2} \rangle \langle \xi_{\alpha_3} \rangle \\ &\quad + \langle \xi_{\alpha_1}, \xi_{\alpha_3} \rangle \langle \xi_{\alpha_2} \rangle + \langle \xi_{\alpha_2}, \xi_{\alpha_3} \rangle \langle \xi_{\alpha_1} \rangle + \langle \xi_{\alpha_1} \rangle \langle \xi_{\alpha_2} \rangle \langle \xi_{\alpha_3} \rangle. \end{aligned} \quad (2.1.13)$$

This may be written in a shorter form as

$$\langle \xi_{\alpha_1} \xi_{\alpha_2} \xi_{\alpha_3} \rangle = \langle \xi_{\alpha_1}, \xi_{\alpha_2}, \xi_{\alpha_3} \rangle + (3) \langle \xi_{\alpha_1}, \xi_{\alpha_2} \rangle \langle \xi_{\alpha_3} \rangle + \langle \xi_{\alpha_1} \rangle \langle \xi_{\alpha_2} \rangle \langle \xi_{\alpha_3} \rangle. \quad (2.1.14)$$

Here the number 3 in parentheses indicates the number of terms of the same type; they differ only in the order of subscripts. Further, we have

$$\begin{aligned} \langle \xi_{\alpha_1} \dots \xi_{\alpha_4} \rangle &= \langle \xi_{\alpha_1}, \xi_{\alpha_2}, \xi_{\alpha_3}, \xi_{\alpha_4} \rangle + (3) \langle \xi_{\alpha_1}, \xi_{\alpha_2} \rangle \langle \xi_{\alpha_3}, \xi_{\alpha_4} \rangle \\ &\quad + (4) \langle \xi_{\alpha_1}, \xi_{\alpha_2}, \xi_{\alpha_3} \rangle \langle \xi_{\alpha_4} \rangle + (6) \langle \xi_{\alpha_1}, \xi_{\alpha_2} \rangle \langle \xi_{\alpha_3} \rangle \langle \xi_{\alpha_4} \rangle \\ &\quad + \langle \xi_{\alpha_1} \rangle \langle \xi_{\alpha_2} \rangle \langle \xi_{\alpha_3} \rangle \langle \xi_{\alpha_4} \rangle. \end{aligned} \quad (2.1.15)$$

Formulas (2.1.14, 15) have the following characteristic feature: on the right-hand side there are all possible terms (without non-unity numerical factor) that are different despite the symmetry of correlators and products and that correspond to various divisions of the elements $\xi_{\alpha_1}, \dots, \xi_{\alpha_s}$ into subgroups; moreover, a correlator corresponds to each subgroup. The formulas for moments of higher orders $\langle \xi_{\alpha_1} \dots \xi_{\alpha_s} \rangle, s > 4$ have the same feature. This gives a simple rule for writing any of these formulas without using (2.1.11).

It should be noted that the above-mentioned rule (all combinations that yield noncoincident terms must be taken into account but only once) is valid when we calculate more complex correlators, i.e. express them in terms of simple correlators.

For example,

$$\begin{aligned}
 \langle \xi_1 \xi_2, \xi_3 \xi_4 \rangle &= \langle \xi_1, \xi_2, \xi_3, \xi_4 \rangle + \langle \xi_1, \xi_2, \xi_3 \rangle \langle \xi_4 \rangle \\
 &\quad + \langle \xi_1, \xi_2, \xi_4 \rangle \langle \xi_3 \rangle + \langle \xi_1, \xi_3, \xi_4 \rangle \langle \xi_2 \rangle \\
 &\quad + \langle \xi_2, \xi_3, \xi_4 \rangle \langle \xi_1 \rangle + \langle \xi_1, \xi_3 \rangle \langle \xi_2, \xi_4 \rangle \\
 &\quad + \langle \xi_1, \xi_4 \rangle \langle \xi_2, \xi_3 \rangle + \langle \xi_1, \xi_3 \rangle \langle \xi_2 \rangle \langle \xi_4 \rangle \\
 &\quad + \langle \xi_1, \xi_4 \rangle \langle \xi_2 \rangle \langle \xi_3 \rangle + \langle \xi_2, \xi_3 \rangle \langle \xi_1 \rangle \langle \xi_4 \rangle \\
 &\quad + \langle \xi_2, \xi_4 \rangle \langle \xi_1 \rangle \langle \xi_3 \rangle. \tag{2.1.16}
 \end{aligned}$$

Each of the diagrams in Fig. 2.1 corresponds to one particular term on the right-hand side of (2.1.16). The element groups that are divided by commas on the left-hand side of (2.1.16) are surrounded by dotted lines in the diagram. In this example we have two groups of two elements in each group. In the general case the number of groups and the number of elements in them can be arbitrary. The subset of elements that are enclosed within a solid line in each diagram corresponds to the correlator multiplier in the appropriate term on the right-hand side of (2.1.16). We should not take into account diagrams having a group of elements which is not connected with other groups by solid lines.

The above-mentioned rule, which is not difficult to understand, is very useful in calculations.

The random variables ξ_1, \dots, ξ_n are called Gaussian if all correlators except $\langle \xi_\alpha \rangle, \langle \xi_\alpha, \xi_\beta \rangle, \alpha, \beta = 1, \dots, n$ are equal to zero. According to (2.1.10), we have for them:

$$\Theta(v) = \exp \left\{ \sum_{\alpha} \langle \xi_{\alpha} \rangle v_{\alpha} + \frac{1}{2} \sum_{\alpha, \beta} \langle \xi_{\alpha}, \xi_{\beta} \rangle v_{\alpha} v_{\beta} \right\}. \tag{2.1.17}$$

Carrying out the Fourier transformation that is the inverse of (2.1.2) and using

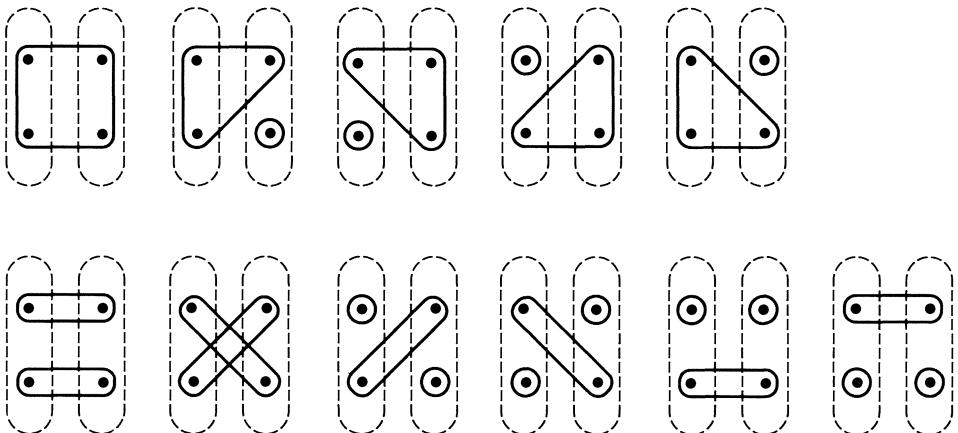


Fig. 2.1. Diagrams corresponding to each of the 11 terms on the right-hand side of (2.1.16)

(2.1.17), we easily obtain for this case

$$w(\xi) = (2\pi)^{-n/2} \det^{1/2} \|D_{\alpha\beta}\| \exp \left[-\frac{1}{2} \sum_{\alpha,\beta} D_{\alpha\beta} (\xi_\alpha - m_\alpha)(\xi_\beta - m_\beta) \right], \quad (2.1.18)$$

where

$$m_\alpha = \langle \xi_\alpha \rangle, \quad \|D_{\alpha\beta}\| = \|\langle \xi_\alpha, \xi_\beta \rangle\|^{-1}. \quad (2.1.19)$$

Clearly, formulas (2.1.14–16) are significantly simpler in the case of Gaussian random variables.

2.1.3 Moments and Correlators in Quantum Theory

The above formulas are valid in the nonquantum case. However, it should be noted that random variables become operators in the quantum case and, generally speaking, they are noncommutative. Therefore, products with different order of multipliers are distinct in the quantum case. All of them correspond to the same nonquantum product. Hence, moments and, consequently, cumulants may be defined in various ways in the quantum case.

In order to extend the above formulas to the quantum case, it is first of all necessary to introduce a certain principle of operator ordering. Let us consider two special ordering principles.

The first ordering principle. We denote the operator by the sign $\hat{}$ above the letter. In all expressions, let the operators be arranged in such a way that an operator with a smaller subscript should stand to the left of an operator with a larger subscript. For this ordering the probability density and the characteristic function are defined by

$$\begin{aligned} w(\xi_1, \dots, \xi_n) &= \langle \delta(\hat{\xi}_1 - \xi_1) \dots \delta(\hat{\xi}_n - \xi_n) \rangle \\ &\equiv \text{Tr} \{ \delta(\hat{\xi}_1 - \xi_1) \dots \delta(\hat{\xi}_n - \xi_n) \hat{\rho} \}, \end{aligned} \quad (2.1.20a)$$

$$\Theta(v_1, \dots, v_n) = \langle \exp(v_1 \hat{\xi}_1) \dots \exp(v_n \hat{\xi}_n) \rangle, \quad (2.1.20b)$$

where ρ is the density matrix describing the system state.

From the various types of moments one should take the moments with due ordering, for example $\langle \hat{\xi}_2 \hat{\xi}_3 \rangle$, $\langle \hat{\xi}_1 \hat{\xi}_3 \hat{\xi}_5 \rangle$ and so on, but not the moments $\langle \hat{\xi}_3 \hat{\xi}_2 \rangle$, $\langle \hat{\xi}_3 \hat{\xi}_1 \hat{\xi}_5 \rangle$. In this case the formulas (2.1.12–15) retain their validity. Formulas of the type (2.1.16) are also valid.

The second principle: Symmetrization ordering. Instead of (2.1.20b), we now define the characteristic function in the following way:

$$\Theta(v_1, \dots, v_n) = \left\langle \exp \left(\sum_{\alpha=1}^n v_\alpha \hat{\xi}_\alpha \right) \right\rangle. \quad (2.1.21)$$

Substituting (2.1.21) into (2.1.3), we obtain the expressions

$$\begin{aligned} \langle \hat{\xi}_\alpha \hat{\xi}_\beta \rangle^{(s)} &= \frac{1}{2} \langle \hat{\xi}_\alpha \hat{\xi}_\beta + \hat{\xi}_\beta \hat{\xi}_\alpha \rangle, \\ \langle \hat{\xi}_\alpha \hat{\xi}_\beta \hat{\xi}_\gamma \rangle^{(s)} &= \frac{1}{6} \langle \hat{\xi}_\alpha \hat{\xi}_\beta \hat{\xi}_\gamma + \hat{\xi}_\alpha \hat{\xi}_\gamma \hat{\xi}_\beta + \hat{\xi}_\beta \hat{\xi}_\alpha \hat{\xi}_\gamma + \hat{\xi}_\beta \hat{\xi}_\gamma \hat{\xi}_\alpha + \hat{\xi}_\gamma \hat{\xi}_\alpha \hat{\xi}_\beta + \hat{\xi}_\gamma \hat{\xi}_\beta \hat{\xi}_\alpha \rangle, \\ &\vdots \end{aligned} \quad (2.1.22)$$

These are called the symmetrized moments. The superscript (s) on the left-hand side of (2.1.22) indicates that the moments correspond to the symmetrization ordering. All formulas of nonquantum theory are valid for every ordering principle. Of course, other ordering principles are also possible.

2.2 Some Results of Equilibrium Statistical Thermodynamics

2.2.1 Entropy and Free Energy

Let us consider a physical system S which is characterized by a Hamiltonian function $\mathcal{H}(z)$ in the nonquantum case. Here $z = (q, p) = (q_1, \dots, q_n, p_1, \dots, p_n)$ are the dynamic variables, namely, the set of coordinates and momenta of the system S. The equilibrium joint probability density of dynamic variables is denoted by $w(z)$.

The average Hamiltonian function is called the internal energy

$$U = \langle \mathcal{H}(z) \rangle \equiv \int \mathcal{H}(z) w(z) dz . \quad (2.2.1)$$

The entropy of the state is defined by

$$S = -k \int w(z) \ln [w(z)] dz . \quad (2.2.2)$$

It is a measure of uncertainty in the system, a measure of the total statistical disorder. The quantity $k = k_B$ in (2.2.2) is the Boltzmann constant. Formula (2.2.2) is nonquantum; it leaves the additive constant uncertain. The expression

$$F = U - TS \quad (2.2.3)$$

is called the free energy. According to (2.2.1, 2), it may be written as

$$F(T) = \int [\mathcal{H}(z) + kT \ln w(z)] w(z) dz . \quad (2.2.4)$$

In statistical physics two main equilibrium probability distributions are important: the canonical or Gibbs distribution

$$w(z) = C_1 \exp[-\mathcal{H}(z)/kT], \quad C_1^{-1} = \int \exp[-\mathcal{H}/kT] dz , \quad (2.2.5)$$

and the microcanonical distribution

$$w(z) = C_2 \delta(\mathcal{H}(z) - E), \quad C_2^{-1} = \int \delta(\mathcal{H}(z) - E) dz . \quad (2.2.6)$$

If the system S is large and complex, i.e. if it consists of a very large number of molecules, atoms, ions, etc., then both (2.2.5) and (2.2.6) can be applied to it. Any distribution applied to the large system yields the same distribution (namely, the Gibbs distribution) for a subsystem S_1 that is much smaller than the system S.

If the system S is small and simple and if it is in thermal contact with some ambient systems that have the temperature T (taken together, they are called “the thermostat”), then only (2.2.5) is valid for the system S. If “the thermostat” is included in the system under study, both distributions (2.2.5, 6) can be used again.

As a consequence of the two versions of the equilibrium probability distribution, two versions of nonequilibrium thermodynamics are possible. The first one is the Gibbs’ or the free energy version and the second one is the microcanonical or the entropy version. We will regard the Gibbs’ version as the main one and the entropy version as a modified one. The terms “main” and “modified” are used to make the distinction and they can be interchanged.

In the Gibbs’ version, substituting (2.2.5) into (2.2.4) gives

$$F = -kT \ln \int \exp[-\mathcal{H}(z)/kT] dz . \quad (2.2.7)$$

In the microcanonical version it is convenient to replace (2.2.6) by the approximate formula

$$w(z) = C_\varepsilon g_\varepsilon(\mathcal{H}(z) - E), \quad C_\varepsilon^{-1} = \int g_\varepsilon(\mathcal{H}(z) - E) dz , \quad (2.2.8)$$

where $\varepsilon > 0$ is a very small quantity and

$$g_\varepsilon(x) = \begin{cases} 1 & \text{for } |x| \leq \varepsilon , \\ 0 & \text{for } |x| > \varepsilon . \end{cases} \quad (2.2.9)$$

Substituting (2.2.8) into (2.2.4), we find $F = E - TS$, where

$$\begin{aligned} S &= k \ln \int g_\varepsilon(\mathcal{H}(z) - E) dz \\ &= -k \ln C_\varepsilon . \end{aligned} \quad (2.2.10)$$

Since the additive constant in (2.2.2, 10) is uncertain, the free energy F is determined to an accuracy of the term $\text{const} \cdot T$, where the constant may depend on ε .

2.2.2 Thermodynamic Parameters. The First Law of Thermodynamics

By definition, any function $B_\alpha(z)$, $z = (q, p)$ that has a macroscopic character can serve as a random internal thermodynamic parameter. The mean value $\langle B_\alpha(z) \rangle = A_\alpha$ is called a mean internal thermodynamic parameter. In some cases the internal parameters have the sense of the order parameters. The parameters on which the equilibrium probability density $w(z)$ can depend are called the external thermodynamic parameters.

Suppose that the Hamiltonian function $\mathcal{H}(z, a)$ depends on parameters $a = (a_1, \dots, a_r)$. Substituting this function into (2.2.5), we come to the conclusion that in Gibbs’ version the external thermodynamic parameters are T, a_1, \dots, a_r , and in the microcanonical version these parameters are E, a_1, \dots, a_r .

Let the Gibbs external parameters vary a little. We denote their small variations by dT, da_1, \dots, da_r . The variation of parameters leads to the following variation

of the Hamiltonian function

$$\delta\mathcal{H}(z, a) = \sum_{\alpha=1}^r (\partial\mathcal{H}(z, a)/\partial a_\alpha) da_\alpha . \quad (2.2.11)$$

Let us find the variation of the free energy induced by these parameter variations. According to (2.2.7), we have

$$dF = -kT d \ln \int \exp[-\mathcal{H}(z, a)/kT] dz - k dT \ln \int \exp[-\mathcal{H}(z, a)/kT] dz . \quad (2.2.12)$$

Obviously,

$$\begin{aligned} d \ln \int \exp(-\mathcal{H}/kT) dz &= \left[\int \exp(-\mathcal{H}/kT) dz \right]^{-1} \\ &\times \int \exp(-\mathcal{H}/kT) \left[\frac{\mathcal{H}}{kT^2} dT - \frac{\delta\mathcal{H}}{kT} \right] dz . \end{aligned} \quad (2.2.13)$$

By virtue of (2.2.5) the right-hand side of this equation can be written as

$$\int \left[\frac{\mathcal{H}}{kT^2} dT - \frac{\delta\mathcal{H}}{kT} \right] w(z) dz = \frac{U}{kT^2} dT - \frac{\langle \delta\mathcal{H} \rangle}{kT} . \quad (2.2.14)$$

Considering (2.2.11, 14), we can write the variation (2.2.12) in the form

$$dF = (F - U) T^{-1} dT + \sum_{\alpha=1}^r \langle \partial\mathcal{H}(z, a)/\partial a_\alpha \rangle da_\alpha . \quad (2.2.15)$$

It is convenient to denote

$$-\partial\mathcal{H}(z, a)/\partial a_\alpha = B_\alpha(z, a) , \quad (2.2.16a)$$

$$\langle B_\alpha \rangle = A_\alpha , \quad (2.2.16b)$$

$B_\alpha(z)$ being the random internal parameters and A_α , the mean internal parameters. Then equation (2.2.15) will have the form

$$dF = -S dT - \sum_{\alpha=1}^r A_\alpha da_\alpha . \quad (2.2.17)$$

Here the first term on the right-hand side has been simplified by (2.2.3). Using (2.2.3), from (2.2.17) we can find the internal energy variation

$$dU = T dS - \sum_{\alpha=1}^r A_\alpha da_\alpha . \quad (2.2.18)$$

Equations (2.2.17, 18) are valid for the equilibrium (or reversible) processes since the equilibrium probability density (2.2.5) has been used. For the equilibrium process $T dS$ is simply the heat dQ reaching the system. Therefore, (2.2.18) can also be written in the well-known form

$$dQ = dU + \sum_{\alpha=1}^r A_\alpha da_\alpha . \quad (2.2.19)$$

Any of the equations (2.2.17–19) formulates the first law of thermodynamics. As is well known, a variety of results may be obtained from these equations. In particular, from (2.2.17) we get

$$S(T, a) = -\partial F(T, a)/\partial T, \quad (2.2.20a)$$

$$A_\alpha(T, a) = -\partial F(T, a)/\partial a_\alpha. \quad (2.2.20b)$$

2.2.3 The Second Law of Thermodynamics

Up to now we have considered only equilibrium states and processes. However, it should be noted that (2.2.1–3) are also valid for nonequilibrium states, and the formula (2.2.19) expressing the law of energy conservation is valid for all processes including nonequilibrium ones.

Nonequilibrium thermodynamic processes evolve in time in accordance with the second law of thermodynamics. Let us give several formulations appropriate to different processes.

The first formulation. Only processes for which $dS \geq 0$ are possible in the absence of heat exchange, i.e. at $dQ = 0$.

The second formulation. The processes for which

$$dS \geq dQ/T \quad (2.2.21)$$

are the only possible ones. Here the equality sign refers to the equilibrium processes. It may be recalled that a process is called an equilibrium process if all intermediate states are those of thermodynamic equilibrium.

Substituting (2.2.19) into (2.2.21) gives

$$dU - T dS \leq - \sum_{\alpha=1}^r A_\alpha da_\alpha. \quad (2.2.22)$$

For the isothermal processes when T is constant ($dT = 0$), by virtue of (2.2.3) we have

$$dU - T dS = dF + S dT = dF. \quad (2.2.23)$$

Therefore, inequality (2.2.22) takes the form

$$dF \leq - \sum_{\alpha=1}^r A_\alpha da_\alpha. \quad (2.2.24)$$

Hence, we obtain *the third formulation*: for the isothermal process the free energy cannot increase if, in addition, all external parameters a_α are constant.

2.2.4 Characteristic Function of Internal Parameters and Free Energy

Let us call the external parameters natural if $\ln w_0(z)$ (where $w_0(z)$ is the Gibbs distribution) depends on the corresponding internal parameter linearly. From (2.2.5) we see that T is not a natural parameter, whereas T^{-1} and $\beta = (kT)^{-1}$ are.

Suppose that $a = (a_1, \dots, a_r)$ are natural parameters. Then, using (2.2.16a), we can write the Hamiltonian function in the form

$$\begin{aligned}\mathcal{H}(z, a) &= \mathcal{H}_0(z) - \sum B_\alpha(z) a_\alpha \\ &\equiv \mathcal{H}_0(z) - B(z) a,\end{aligned}\quad (2.2.25)$$

where $\mathcal{H}_0(z)$ is another function. Substituting (2.2.25) into (2.2.7) gives

$$\exp[-\beta F(a)] = \int \exp[-\beta \mathcal{H}_0(z) + \beta a B(z)] dz. \quad (2.2.26)$$

Here we have taken into account that F depends on a .

Using (2.2.5) with the Hamiltonian function (2.2.25), we can find the characteristic function (2.1.2) of the internal parameters:

$$\begin{aligned}\Theta(v) &= \int \exp[v B(z)] w_0(z) dz \\ &= \left[\int \exp(-\beta \mathcal{H}_0 + \beta a B) dz \right]^{-1} \int \exp[-\beta \mathcal{H}_0(z) + (\beta a + v) B(z)] dz.\end{aligned}\quad (2.2.27)$$

Using (2.2.26) and in one case replacing a by $(a + kTv)$ and in the other case leaving a unchanged, we write (2.2.27) in the form

$$\Theta(v) = \exp[-\beta F(a + kTv) + \beta F(a)]. \quad (2.2.28)$$

Thus, we have obtained the characteristic function describing the equilibrium fluctuations of random internal parameters expressed in terms of the free energy as a function of the natural external parameters. One can, therefore, express both the equilibrium moments [according to (2.1.3)] and the correlators [formula (2.1.6)] of random internal parameters in terms of the free energy $F(a)$. Thus, substituting (2.2.28) into (2.1.6), we obtain the expression for the correlators:

$$\langle B_{\alpha_1}, \dots, B_{\alpha_m} \rangle = -\beta \left[\frac{\partial^m F(a + kTv)}{\partial v_{\alpha_1} \dots \partial v_{\alpha_m}} \right]_{v=0} \quad (2.2.29)$$

or

$$\langle B_{\alpha_1}, \dots, B_{\alpha_m} \rangle = -(kT)^{m-1} \frac{\partial^m F(a)}{\partial a_{\alpha_1} \dots \partial a_{\alpha_m}}. \quad (2.2.30)$$

In particular, setting $m = 1$ we obtain (2.2.20b). If we set $m = 2$, we get

$$\langle B_\alpha, B_\beta \rangle = -kT \partial^2 F(a)/\partial a_\alpha \partial a_\beta. \quad (2.2.31)$$

The correlation matrix $\langle B_\alpha, B_\beta \rangle$ is nonnegative definite since

$$\sum_{\alpha, \beta} \langle B_\alpha, B_\beta \rangle c_\alpha c_\beta = \left\langle \sum_\alpha B_\alpha c_\alpha, \sum_\beta B_\beta c_\beta \right\rangle \geq 0 \quad (2.2.32)$$

for any real vector $c = (c_1, \dots, c_r)$. Consequently, the matrix of the second

derivatives $\partial^2 F / \partial a_\alpha \partial a_\beta$ is nonpositive definite. This means that function $F(a)$ is a concave function of the variables a .

2.2.5 Thermodynamic Potential $\Gamma(\alpha)$

The function $\mathcal{H}_0(z) = B_0(z)$ in (2.2.25), like the other functions, is a random internal parameter. Unfortunately, formula (2.2.30) cannot serve as a basis for calculating the correlators including $\mathcal{H}_0(z)$. In order to calculate the correlators of this function along with other parameters, the theory of the preceding section must be modified.

Let us introduce the following notations for the external parameters:

$$\alpha_0 = -1/T, \quad \alpha_1 = a_1/T, \quad \dots, \quad \alpha_r = a_r/T. \quad (2.2.33)$$

The thermodynamic potential as a function of these parameters is defined by

$$\Gamma(\alpha) = F(T(\alpha_0), a(\alpha))/T(\alpha_0) \quad \alpha = (\alpha_0, \alpha_1, \dots, \alpha_r). \quad (2.2.34)$$

Then, instead of (2.2.26), we will have

$$\exp[-\Gamma(\alpha)/k] = \int \exp \left[\sum_{i=0}^r \alpha_i B_i(z)/k \right] dz. \quad (2.2.35)$$

Here the parameters α_i must run only through the values at which the integral on the right-hand side converges.

According to (2.2.33, 34), the Gibbs formula

$$w_0(z) = \exp[\beta F - \beta \mathcal{H}_0(z) + \beta a B(z)]$$

takes the form

$$w_0(z) = \exp \left\{ k^{-1} \left[\Gamma(\alpha) + \sum_{i=0}^r \alpha_i B_i(z) \right] \right\}. \quad (2.2.36)$$

Substituting (2.2.36) into

$$\Theta(z) = \int \exp \left[\sum_{i=0}^r v_i B_i(z) \right] w_0(z) dz,$$

instead of (2.2.28), we have

$$\Theta(v) = \exp[-\Gamma(\alpha + kv)/k + \Gamma(\alpha)/k]. \quad (2.2.37)$$

Now, the application of (2.1.6) gives

$$\langle B_{i_1}, \dots, B_{i_m} \rangle = -k^{m-1} \partial^m \Gamma(\alpha)/\partial \alpha_{i_1} \dots \partial \alpha_{i_m}. \quad (2.2.38)$$

Here i_1, \dots, i_m run through the values $0, 1, \dots, r$. Consequently, unlike (2.2.30), this formula can determine the correlators including $\mathcal{H}(z)$ and, therefore, the energy (2.2.25).

In (2.2.30, 38) the Boltzmann constant $k = 1.38 \times 10^{-23}$ J/K is a small quantity from the macroscopic point of view. Therefore, the equilibrium correlators $\langle B_{i_1}, \dots, B_{i_m} \rangle$ of the internal parameters are relatively small for $m > 1$, and they progressively decrease with increasing m . For observing the fluctuations of internal parameters in reality one needs amplifiers.

If the potential Γ is used instead of the free energy, the first law of thermodynamics (2.2.17) takes the form

$$d\Gamma = - \sum_{i=0}^r A_i d\alpha_i \equiv U_0 d(T^{-1}) - \sum_{i=1}^r A_i d\alpha_i , \quad (2.2.39)$$

where $A_0 = U_0 = \langle \mathcal{H}_0(z) \rangle$. Substituting

$$\begin{aligned} \Gamma &= U/T - S \\ &= - \sum_{i=0}^r A_i \alpha_i - S \end{aligned} \quad (2.2.40)$$

into the left-hand side of (2.2.39) gives

$$dS = - \sum_{i=0}^r \alpha_i dA_i \equiv T^{-1} dU_0 - \sum_{i=1}^r \alpha_i dA_i . \quad (2.2.41)$$

The validity of these formulas is not restricted by the condition of natural external parameters a_1, \dots, a_r . The formulas (2.2.39, 41) can be regarded as another formulation of the first law of thermodynamics, and (2.2.38) can be regarded as the k -version of (2.2.30).

To conclude this section we remark that in the presence of the parameter $\mathcal{H}_0(z) = B_0(z)$ among the parameters B , one can proceed otherwise; namely, instead of (2.2.25), one can assume that

$$\mathcal{H}(z, a) = \mathcal{H}_0 - \mathcal{H}_0(z)a_0 - \sum_{\alpha=1}^r B_\alpha(z)a_\alpha , \quad (2.2.42)$$

where a_0 is the additional parameter conjugate to $\mathcal{H}_0(z)$. Then the correlators of all $B_i(z)$, including $B_0(z)$, can be calculated by (2.2.30). However, in this case among external parameters T, a_0, a_1, \dots, a_r there is a surplus one. In fact, substituting (2.2.42) into (2.2.7) gives

$$F = -kT \ln \int \exp \left[-\beta(1-a_0)\mathcal{H}_0 + \sum_{\alpha=1}^r \beta a_\alpha B_\alpha(z) \right] dz . \quad (2.2.43)$$

We see that the free energy F depends on the combinations $T/(1-a_0)$, a_α/T , but not on T, a_0 and a_α separately. The use of the potential Γ is therefore preferable.

2.2.6 Conditional Entropy

Let us return to the general case when the external parameters are not necessarily the natural ones. The probability density of the internal parameters $B(z) = (B_1(z), \dots, B_r(z))$ and, analogously, of $(B_0(z), B_1(z), \dots, B_r(z))$ is defined by

$$w(B) = \int \delta(B - B(z)) w(z) dz , \quad (2.2.44)$$

where $\delta(x) = \delta(x_1) \dots \delta(x_r)$.

In addition to $B(z)$ we introduce the set of variables $\zeta(z)$ [2.1], so that the modulus of the Jacobian of the transformation $z \rightarrow (B, \zeta)$ be equal to unity. Then

the joint probability density for B and ζ is expressed by

$$w(B, \zeta) = w(z(B, \zeta)). \quad (2.2.45)$$

We introduce the conditional probability density

$$w(\zeta|B) = \frac{w(B, \zeta)}{w(B)}, \quad (2.2.46)$$

which essentially describes the probability density on the hypersurface defined by the equation $B(z) = B$, i.e. $B_1(z) = B_1, \dots, B_r(z) = B_r$ (B_1, \dots, B_r are fixed).

The conditional probability density (2.2.46), which corresponds to the fixed values of B , determines the conditional entropy $S(B)$ according to the formula

$$S(B) = -k \int w(\zeta|B) \ln [w(\zeta|B)] d\zeta, \quad (2.2.47)$$

which is analogous to the formula (2.2.2) defining the nonconditional, i.e. ordinary, entropy S .

We also introduce the mean conditional entropy

$$S_{\zeta|B} = \langle S(B) \rangle \equiv \int S(B) w(B) dB, \quad (2.2.48)$$

and we will find the relation between the conditional and the nonconditional entropies. Substituting (2.2.47) into (2.2.48) gives

$$S_{\zeta|B} = -k \int w(\zeta|B) w(B) \ln [w(\zeta|B)] d\zeta dB. \quad (2.2.49)$$

Considering (2.2.46) we obtain

$$\begin{aligned} S_{\zeta|B} &= -k \int w(B, \zeta) [\ln w(B, \zeta) - \ln w(B)] dB d\zeta \\ &= S - S_B, \end{aligned} \quad (2.2.50)$$

where S is defined by (2.2.2) and S_B is defined by

$$S_B = -k \int w(B, \zeta) \ln [w(B)] dB d\zeta. \quad (2.2.51)$$

Since

$$\int w(B, \zeta) d\zeta = w(B), \quad (2.2.52)$$

equation (2.2.51) can be written in the form

$$S_B = -k \int w(B) \ln [w(B)] dB. \quad (2.2.53)$$

Thus, we have

$$S = S_B + S_{\zeta|B}. \quad (2.2.54)$$

The last equation can be interpreted in the following way. The entropy is a measure of the statistical disorder; S describes the complete disorder in the system, namely, the disorder of all dynamic variables; S_B describes the disorder of the values of random internal parameters B , i.e. the disorder of the position of the hypersurface $B(z) = B$; $S(B)$ describes the disorder of the phase point position on this hypersurface at fixed values of B ; $S_{\zeta|B}$ describes the mean disorder of the position of a point on the hypersurface. It is natural that the disorder of the point position in the phase space is equal to the sum of the disorder of the hypersurface position and the disorder of the point position on the hypersurface.

2.2.7 Formulas Determining the Equilibrium Probability Density of Internal Parameters

Let us obtain the consequences of (2.2.47) in the two versions.

Gibbs' version or the kT -version. Let us take the Gibbs distribution (2.2.5) as the required equilibrium probability density. It can be written as

$$w(z) = \exp\left(\frac{F - \mathcal{H}(z)}{kT}\right). \quad (2.2.55)$$

Using (2.2.45, 46), we find with the help of the above probability density the conditional probability density

$$w(\zeta|B) = \frac{\exp\{(kT)^{-1}[F - \mathcal{H}(B, \zeta)]\}}{w(B)}. \quad (2.2.56)$$

Substituting this into (2.2.47), we obtain

$$S(B) = -k \int \left[\frac{F - \mathcal{H}(B, \zeta)}{kT} - \ln w(B) \right] w(\zeta|B) d\zeta \quad (2.2.57)$$

or

$$S(B) = -\frac{F}{T} + \frac{U(B)}{T} + k \ln w(B), \quad (2.2.58)$$

where

$$U(B) = \int \mathcal{H}(B, \zeta) w(\zeta|B) d\zeta \quad (2.2.59)$$

is the conditional internal energy corresponding to fixed B . We easily verify that the ordinary internal energy (2.2.1) can be obtained by averaging $U(B)$.

The equation

$$F(B) = U(B) - TS(B), \quad (2.2.60)$$

which is analogous to (2.2.3), defines the conditional free energy $F(B)$ corresponding to the fixed values of B . By virtue of (2.2.60) equation (2.2.58) gives

$$w(B) = \exp\left(\frac{F - F(B)}{kT}\right). \quad (2.2.61)$$

Thus, we have demonstrated that the conditional free energy determines the equilibrium probability density of the internal parameters precisely and completely.

The entropy version or the k-version. As the initial equilibrium probability density we now take the probability density (2.2.8), which approximates to the micro-canonical distribution (2.2.6) for small values of ε . By virtue of (2.2.10) formula (2.2.8) can be written as

$$w(z) = e^{-S/k} \vartheta_\varepsilon(\mathcal{H}(z) - E). \quad (2.2.62)$$

Substituting (2.2.62) into (2.2.46) and using (2.2.47), we find

$$\begin{aligned} S(B) = & -k[w(B)]^{-1} \int \left[-\frac{S}{k} + \ln \vartheta_\varepsilon(\mathcal{H}(B, \zeta) - E) - \ln w(B) \right] \\ & \times e^{-S/k} \vartheta_\varepsilon(\mathcal{H}(B, \zeta) - E) d\zeta. \end{aligned} \quad (2.2.63)$$

It is easy to see that $\vartheta_\varepsilon \ln \vartheta_\varepsilon$ is equal to zero in both cases, i.e. when $\vartheta_\varepsilon = 1$ and when $\vartheta_\varepsilon = 0$. Hence, the second term in the square brackets drops out. The terms $-S/k$ and $-\ln w(B)$ do not depend on ζ and can be factored outside the integral sign. Taking into account also that by virtue of (2.2.52)

$$\int e^{-S/k} \vartheta_\varepsilon(\mathcal{H}(B, \zeta) - E) d\zeta = w(B), \quad (2.2.64)$$

we obtain from (2.2.63)

$$w(B) = \exp \left[\frac{-S + S(B)}{k} \right]. \quad (2.2.65)$$

This formula is valid for any ε , however small.

We see that in the entropy version the equilibrium probability density of the internal parameters is determined by the conditional entropy. When the system under study is small and when it is in contact with a thermostat, one should use only formula (2.2.61). If the system is large and complex, one can use any of the formulas (2.2.5, 6) whether or not the system is in contact with a thermostat. This means that the following asymptotic relation

$$[T^{-1}F(B)]_{T=\text{const}} \approx -S(B) + \text{const} \quad (2.2.66)$$

is valid at typical values of the fluctuational deviations $B - B_0$ from equilibrium; these values are determined by the condition $|S(B) - S(B_0)| \sim k$ or $F - F_0 \sim kT$. In (2.2.66) $S(B) = S[B, T(B)]$ and the constants are independent of B .

For a complex system (namely, a system with many degrees of freedom) it is of no importance whether the system is in contact with a thermostat or not since the system itself plays the role of the thermostat.

Example. Let us consider an ideal gas consisting of N identical monatomic molecules and enclosed in a vertical cylindrical vessel which is closed from above by a piston having mass m and unit area. We suppose that the piston can slide without friction in the vessel. The equilibrium position of the piston is determined

by equating the piston weight mg to the gas pressure force $pS = p = kTn$. In our case $p = kTN/V$, where V is the gas volume. When the piston moves freely, the volume V varies spontaneously. Hence, it is an internal parameter. At the same time, the piston coordinate V and the corresponding momentum can be treated as dynamic variables. For this system we can easily calculate the entropy and the internal energy corresponding to the fixed value of V :

$$S(V, T) = kN \ln V + \frac{1}{2}(3N + 1)k \ln T + S_0 , \quad (2.2.67a)$$

$$U(V, T) = \frac{1}{2}(3N + 1)kT + mgV . \quad (2.2.67b)$$

Hence, we find

$$[T^{-1}F(V, T)]_{T=T_0} = -kN \ln V + mgT_0^{-1}V + \text{const} , \quad (2.2.68)$$

where T_0 is the equilibrium value of the temperature and

$$S(V, T(V)) = kN \ln V + \frac{1}{2}(3N + 1)k \ln T(V) + S_0 . \quad (2.2.69)$$

The dependence $T(V)$ is determined by the condition $U(T, V) = \text{const}$, i.e.

$$T - T_0 = -2(3N + 1)^{-1}k^{-1}mg(V - V_0) \quad (2.2.70)$$

(V_0 is the equilibrium volume). For typical fluctuational deviations $V - V_0 \sim N^{-1/2}V_0$ (this estimation is the result of the condition $F - F_0 \sim kT$) it is possible to neglect the nonlinear terms of the expansion of $\ln T(V)$ in $V - V_0$. Thus, we have

$$\begin{aligned} S(V, T(V)) &\approx kN \ln V + \frac{1}{2}(3N + 1)k[\ln T_0 + T_0^{-1}(T - T_0)] + S_0 \\ &= kN \ln V + mgT_0^{-1}(V - V_0) + \text{const} . \end{aligned} \quad (2.2.71)$$

Comparing (2.2.68) with (2.2.71), we see that the approximate equation (2.2.66) is valid. The ratio of the quadratic term to the linear one is equal to $(V - V_0)/V_0 = N^{-1/2}$ in order of magnitude, i.e. it is very small at large values of N . Consequently, in the present case the validity of (2.2.66) is ensured by the condition of very large N .

In analogy with (2.2.34) we can introduce the conditional potential

$$\Gamma(B) = F(B)/T . \quad (2.2.72)$$

Using it we get the following form of (2.2.61):

$$w(B) = \exp\{\Gamma - \Gamma(B)\}/k . \quad (2.2.73)$$

It becomes more similar to the formula (2.2.65) of the entropy version. We see that (2.2.73) transforms into (2.2.65) if we replace Γ by $-S$ and vice versa.

2.2.8 Conditional Thermodynamic Potentials and the First Law of Thermodynamics

Substituting (2.2.47, 59) into (2.2.60), we get

$$F(B) = \int [\mathcal{H}(B, \zeta) + kT \ln w(\zeta|B)] w(\zeta|B) d\zeta . \quad (2.2.74)$$

In Gibbs' version, by virtue of (2.2.56) we have

$$w(\zeta|B) = \frac{1}{Z(B)} \exp\left(-\frac{\mathcal{H}(B, \zeta)}{kT}\right), \quad (2.2.75)$$

where

$$Z(B) = \int \exp[-\beta \mathcal{H}(B, \zeta)] d\zeta \quad (2.2.76)$$

is the factor that ensures the fulfilment of the normalization condition. If we now substitute (2.2.75) into (2.2.74), after factoring the constant outside the integral sign we arrive at

$$F(B) = -kT \ln Z(B). \quad (2.2.77)$$

This equation is completely analogous to the equation for the nonconditional potential

$$F = -kT \ln Z, \quad (2.2.78)$$

where

$$Z = \int \exp[-\beta \mathcal{H}(z)] dz. \quad (2.2.79)$$

The last two equations are equivalent to (2.2.7).

The conditional statistical sum (2.2.76) can be called an incompletely integrated statistical sum since integrating it with respect to B gives the ordinary statistical sum (2.2.79)

$$Z = \int Z(B) dB. \quad (2.2.80)$$

This equation implies the relation between the free energy F and the free energy $F(B)$. In fact, rearranging (2.2.77, 78) to solve for the statistical sums and substituting the expressions obtained into (2.2.80), we have

$$\exp(-\beta F) = \int \exp[-\beta F(B)] dB. \quad (2.2.81)$$

Let us return to the case of the natural external parameters when the Hamiltonian has the form (2.2.25). Substituting (2.2.25) into (2.2.76) gives

$$Z(B) = \exp(\beta aB) Z_0(B), \quad aB = \sum_{\alpha=1}^r a_\alpha B_\alpha, \quad (2.2.82)$$

where

$$Z_0(B) = \int \exp[-\beta \mathcal{H}_0(z)] \delta(B(z) - B) dz. \quad (2.2.83)$$

If we now substitute (2.2.82) into (2.2.77), we will have

$$F(B) = F_0(B) - aB. \quad (2.2.84)$$

Here

$$F_0(B) = -kT \ln Z_0(B). \quad (2.2.85)$$

Substituting (2.2.84) into (2.2.81), we obtain the formula connecting these two free energies:

$$\exp[-\beta F(a)] = \int \exp[\beta aB - \beta F_0(B)] dB. \quad (2.2.86)$$

The transformation (2.2.86) or, more precisely, the corresponding transformation of statistical sums

$$Z(a) = \int \exp(\beta aB) Z_0(B) dB \quad (2.2.87)$$

is the Fourier transformation for pure imaginary $a = iu$. One can easily write the inverse transformations.

As we see from (2.2.85, 83), the conditional free energy $F_0(B)$ is a function of the temperature $T = (k\beta)^{-1}$ and the internal parameters B . Varying these variables and using (2.2.85, 83), we have

$$dF_0(T, B) = -S_0(T, B) dT + \sum_{\alpha=1}^r D_\alpha(T, B) dB_\alpha \quad (2.2.88)$$

(equations (2.2.59, 60) taken at $a = 0$ are also used). Here

$$S_0(T, B) = [S(B)]_{a=0},$$

$$D_\alpha(T, B) = Z_0^{-1} \int \exp[-\beta \mathcal{H}_0(B, \zeta)] \frac{\partial \mathcal{H}_0(B, \zeta)}{\partial B_\alpha} d\zeta. \quad (2.2.89)$$

If the parameters B are fixed, they are nonrandom and coincide with their mean values A . Hence, in this case we can write A instead of B in (2.2.88):

$$dF_0(T, A) = -S_0(T, A) dT + \sum_{\alpha=1}^r D_\alpha(T, A) dA_\alpha. \quad (2.2.90)$$

We can derive the analogous equation in another way, namely, by using the first law of thermodynamics (2.2.17), where the nonconditional free energy, which is a function of T and a , is used. Let us introduce the function $\bar{F}_0(T, A)$, which is obtained from $F(T, a)$ by the Legendre transformation

$$\bar{F}_0(T, A) = F(T, a(A)) + Aa(A), \quad (2.2.91)$$

where the dependence $a(A)$ is the inverse of the dependence $A = -\partial F(a)/\partial a$ [see (2.2.20b)]. Taking the differential of (2.2.91), we have

$$d\bar{F}_0 = dF + a dA + A da \quad (2.2.92)$$

or, if we substitute (2.2.17) here, we get

$$d\bar{F}_0(T, A) = -S(T, A) dT + \sum_{\alpha=1}^r a_\alpha(T, A) dA_\alpha. \quad (2.2.93)$$

Hence, in particular, we have

$$\partial \bar{F}_0(A)/\partial A_\alpha = a_\alpha . \quad (2.2.94)$$

Equation (2.2.93) is one of the formulations of the first law of thermodynamics. We see that its form is very similar to the form (2.2.90) of the conditional potentials. Here we have not just superficial similarity. The integral (2.2.86) can be approximately evaluated by the steepest descent method for large values of β ($kT = \beta^{-1}$ is small). This shows that in zeroth order in the small parameter β^{-1} the transformation (2.2.86) turns into the Legendre transformation

$$F_0(T, A) \approx F(T, a(A)) + Aa(A) . \quad (2.2.95)$$

This will be shown with different notation (κ, x, Ψ, Φ instead of β^{-1}, a, F_0, F) in Appendix 1. In real macroscopic systems the smallness of the parameter $\beta^{-1} = kT$ is explained by the smallness of the Boltzmann constant k from the macroscopic point of view.

When the asymptotic formula (2.2.95) is valid, the potential $\bar{F}_0(T, A)$ coincides with $F_0(T, A)$, and from (2.2.93, 94) we have

$$dF_0(T, A) = -S(T, A) + \sum_{\alpha=1}^r a_\alpha(T, A) dA_\alpha , \quad (2.2.96)$$

i.e. in the given approximation $S_0(T, A)$ and $D(T, A)$ do not differ from $S(T, A)$ and $a_\alpha(T, A)$. Besides, we have

$$\partial F_0(A)/\partial A_\alpha = a_\alpha . \quad (2.2.97)$$

Of course, equations (2.2.96, 97) are not precise; we can find the correction terms for them. If the system of interest is microscopic, equations (2.2.96, 97) cannot be applied.

From (2.2.20b, 97) we have

$$dA_\alpha = -(\partial^2 F/\partial a_\alpha \partial a_\beta) da_\beta, \quad da_\alpha = (\partial^2 F_0/\partial A_\alpha \partial A_\beta) dA_\beta . \quad (2.2.98)$$

Consequently, the matrix $-\partial^2 F/\partial a_\alpha \partial a_\beta$ is the inverse of the matrix $\partial^2 F_0/\partial A_\alpha \partial A_\beta$, i.e.

$$\left\| \frac{\partial^2 F_0(A)}{\partial A_\alpha \partial A_\beta} \right\| = - \left\| \frac{\partial^2 F(a)}{\partial a_\alpha \partial a_\beta} \right\|^{-1} . \quad (2.2.99)$$

Since the matrix $\partial^2 F(a)/\partial a_\alpha \partial a_\beta$ is nonpositive definite (see Sect. 2.2.4), the matrix $\partial^2 F_0/\partial A_\alpha \partial A_\beta$ is nonnegative definite. Thus,

$$\left\| \frac{\partial^2 F_0(A)}{\partial A_\alpha \partial A_\beta} \right\| = \text{nonneg. def.}, \quad \left\| \frac{\partial^2 F(A)}{\partial a_\alpha \partial a_\beta} \right\| = \text{nonneg. def.} , \quad (2.2.100)$$

i.e. in the framework of the validity of (2.2.97) the conditional free energies are the convex functions in variables A_1, \dots, A_r .

2.2.9 The Functions $S(B)$ and $F(B)$ and the Second Law of Thermodynamics

The random internal parameters $B_\alpha(t)$ as functions of time are random functions, i.e. they change fluctuationally.

If there is no heat exchange between the system and the ambient medium, the entropy $S(a)$ cannot decrease as a consequence of the first formulation of the second law of thermodynamics (Sect. 2.2.3). However, the random entropy $S(B(t))$ changes fluctuationally and can decrease by a quantity of order k . In other words, microviolations of the second law of thermodynamics are possible.

If we take the mean values $A_a(t) = \langle B_a(t) \rangle$ as the arguments of the function $F(B)$, then the corresponding entropy $S(A(t))$ must not decrease. This is expressed by the inequality

$$\frac{d}{dt} S(A(t)) = \frac{\partial S}{\partial A} \frac{dA}{dt} \geq 0 , \quad (2.2.101)$$

which is another formulation of the second law of thermodynamics. The inequality (2.2.101) is valid in the entropy version, i.e. in the case when there is no heat exchange with the environment. When the system is in contact with a thermostat, one should replace (2.2.101) by

$$\frac{d}{dt} F(A(t)) = \frac{\partial F}{\partial A} \frac{dA}{dt} \leq 0 . \quad (2.2.102)$$

This inequality will be proved later (Sect. 4.6).

2.2.10 The Case in which Energy Is an Argument of the Conditional Entropy

If the energy $B_0(z) = \mathcal{H}_0(z)$ is one of the internal parameters $B(z)$, several further formulas of interest can be obtained. In this case the expression $T^{-1}\mathcal{H}(z, a)$, i.e. by virtue of (2.2.25) the equation

$$T^{-1}\mathcal{H}(z, a) = T^{-1}\mathcal{H}_0(z) - \sum_{\gamma=1}^r B_\gamma(z) T^{-1} a_\gamma , \quad (2.2.103)$$

can be written as

$$T^{-1}\mathcal{H}(z, \alpha) = - \sum_{i=0}^r B_i(z) \alpha_i \quad (2.2.104)$$

($\alpha_0 = -T^{-1}$, $\alpha_\gamma = a_\gamma/T$, $\gamma = 1, \dots, r$). Therefore, from (2.2.1, 59) we have

$$T^{-1}U = - \sum_{i=0}^r \langle B_i \rangle \alpha_i \equiv - \sum_{i=0}^r A_i \alpha_i , \quad (2.2.105a)$$

$$T^{-1}U(B) = - \sum_{i=0}^r B_i \alpha_i . \quad (2.2.105b)$$

If in (2.2.61) we pass from the free energy version to the entropy version using (2.2.3, 60), then we obtain

$$w(B) = \exp\{k^{-1}[-S + S(B) + T^{-1}U - T^{-1}U(B)]\} . \quad (2.2.106)$$

Substituting (2.2.105) into (2.2.106), we arrive at the final formula

$$w(B) = \exp\left\{k^{-1}\left[-S + S(B) + \sum_{i=0}^r (B_i - A_i)\alpha_i\right]\right\} , \quad (2.2.107)$$

which is equivalent to (2.2.61) in our case.

Let us introduce the function

$$\bar{S}(A) = - \sum_{i=0}^r A_i \alpha_i(A) - \Gamma(\alpha(A)) , \quad (2.2.108)$$

where the dependence $\alpha(A)$ is the inverse of the dependence $A_i = -\partial\Gamma(\alpha)/\partial\alpha_i$. The last formula resembling (2.2.40) determines the nonconditional entropy $\bar{S}(A)$ as the Legendre transformation of $\Gamma(\alpha)$. Formula (2.2.80) and formulas

$$\Gamma = F/T = -k \ln Z , \quad (2.2.109a)$$

$$\Gamma(B) = F(B)/T = -k \ln Z(B) , \quad (2.2.109b)$$

$$\Gamma(B) = U(B)/T - S(B) = - \sum B_i \alpha_i - S(B) \quad (2.2.110)$$

imply the formula

$$\begin{aligned} \exp[-k^{-1}\Gamma(\alpha)] &= \int \exp[-k^{-1}\Gamma(B)] dB \\ &= \int \exp\{k^{-1}[\sum B_i \alpha_i + S(B)]\} dB . \end{aligned} \quad (2.2.111)$$

One can obtain from (2.2.111) (see Appendix 1) that, asymptotically, the transformation between $S(B)$ and $\Gamma(\alpha)$ is a Legendre transformation (owing to smallness of k). Consequently, the function (2.2.108) asymptotically coincides with the function $S(B)$ at $B = A$, i.e. $\bar{S}(B) \approx S(B)$. Hence, the asymptotic formula

$$\alpha_i(B) = -\frac{\partial S(B)}{\partial B_i} \quad (2.2.112)$$

is valid in addition to the precise formula $\alpha_i(A) = -\partial\bar{S}(A)/\partial A_i$ following from (2.2.108). Formula (2.2.112) is the k -version of (2.2.97) while (2.2.111) is the k -version of (2.2.86).

2.2.11 Formulas of Quantum Equilibrium Statistical Thermodynamics

The preceding consideration relates to the nonquantum case. In the quantum case one should take the Hamiltonian operator $\hat{\mathcal{H}}$ and the density matrix $\hat{\rho}$ instead of the Hamiltonian function and probability density in phase space. The above-mentioned operators are Hermitian; $\hat{\rho}$ is nonnegative definite. Instead of (2.2.1, 2), we have

$$U = \text{Tr}\{\hat{\mathcal{H}}\hat{\rho}\} , \quad (2.2.113)$$

$$S = -k \text{Tr}\{\hat{\rho}\ln\hat{\rho}\} , \quad (2.2.114)$$

Here $\text{Tr}\{A\}$ means the trace, i.e. the sum of the diagonal elements of the matrix A . It must be noted that unlike (2.2.2), formula (2.2.114) leaves no uncertainty in the choice of the additive constant.

Formula (2.2.3) remains unchanged. In the quantum version the equilibrium distributions (2.2.5, 6) take the form

$$\hat{\rho} = C_1 \exp(-\hat{\mathcal{H}}/kT) \quad (C_1^{-1} = \text{Tr}\{\exp(-\hat{\mathcal{H}}/kT)\}), \quad (2.2.115)$$

$$\hat{\rho} = C_2 \delta(\hat{\mathcal{H}} - E) \quad (C_2^{-1} = \text{Tr}\{\delta(\hat{\mathcal{H}} - E)\}). \quad (2.2.116)$$

Using (2.2.3, 113–115) in the same way, we can obtain the formula

$$F = -kT \ln[\text{Tr}\{\exp(-\hat{\mathcal{H}}/kT)\}], \quad (2.2.117)$$

which is analogous to (2.2.7).

The random internal parameters are defined as operators $\hat{B}_1, \dots, \hat{B}_r$ having macroscopic character. The theory of Sect. 2.2.2 is transferred to the quantum case by replacing an integral in phase space by a trace. In Sect. 2.2.3 there is no need for changes. In the quantum case formulas (2.2.28, 30) of Sect. 2.2.4 (and corresponding formula (2.2.38) of Sect. 2.2.5 for $m > 1$) are not valid even in the case of the symmetrized operator ordering defined by a characteristic function of the type (2.1.20). The reason is that the operator product

$$\exp(-\beta\hat{\mathcal{H}}_0 + \beta a\hat{B}) \exp(v\hat{B})$$

is not generally equal to the expression

$$\exp(-\beta\hat{\mathcal{H}}_0 + \beta a\hat{B} + v\hat{B})$$

since the operators $\hat{\mathcal{H}}_0, \hat{B}_1, \dots, \hat{B}_r$ are generally noncommutative. The conditional entropy analogous to the entropy considered in Sect. 2.2.6 cannot be uniquely defined in the quantum case since in quantum theory there are no general and unique concepts of conditional probabilities and of conditional density matrix. According to this, formulas (2.2.61, 65) have only asymptotic nonquantum sense. Formulas (2.2.95, 97) are valid only when both fluctuational and quantum effects are neglected. Formulas (2.2.91, 94) are valid without restrictions.

2.3 The Markov Random Process and Its Master Equation

2.3.1 Definition of a Markov Process

Let $y(t) = (y_1(t), \dots, y_r(t))$ be an r -component process. It is described by the set of many-time probability densities

$$w(y(t)), w(y(t_1), y(t_2)), \dots, w(y(t_1), \dots, y(t_n)), \dots$$

Let us introduce the many-time conditional probability densities. Generally, the conditional probability density $w(\xi|\eta)$, i.e. the probability density of the random variable ξ at the fixed value of η , is defined by

$$w(\xi, \eta) = w(\xi|\eta)w(\eta) \quad (2.3.1)$$

[see also (2.2.46)]. Putting $\xi = y(t_2)$ and $\eta = y(t_1)$, according to (2.3.1) we obtain

$$w(y(t_1), y(t_2)) = w(y(t_1)) w(y(t_2)|y(t_1)). \quad (2.3.2)$$

Furthermore, setting $\xi = y(t_3)$, $\eta = (y(t_2), y(t_1))$, we find from (2.3.1)

$$w(y(t_1), y(t_2), y(t_3)) = w(y(t_1), y(t_2)) w(y(t_3)|y(t_1), y(t_2)) \quad (2.3.3)$$

or

$$w(y(t_1), y(t_2), y(t_3)) = w(y(t_1)) w(y(t_2)|y(t_1)) w(y(t_3)|y(t_1), y(t_2)) \quad (2.3.4)$$

if we also use (2.3.2). The probability density $w(y(t_1), \dots, y(t_4))$ and other many-time probability densities can be represented in the form of products in the same way. The general formula is of the form

$$\begin{aligned} w(y(t_1), \dots, y(t_n)) &= w(y(t_1)) w(y(t_2)|y(t_1)) w(y(t_3)|y(t_1), y(t_2)) \dots \\ &\times w(y(t_n)|y(t_1), \dots, y(t_{n-1})). \end{aligned} \quad (2.3.5)$$

Let us suppose that $t_1 < t_2 < \dots < t_n$. A process is called a Markov process if for any k the equation

$$w(y(t_k)|y(t_1), \dots, y(t_{k-1})) = w(y(t_k)|y(t_{k-1})) \quad (2.3.6)$$

is valid no matter what t_1, \dots, t_k are. It is only important that they must be ordered, i.e. the inequality $t_1 < t_2 < \dots < t_k$ must be valid. Equation (2.3.6) means that the conditional probability density depends only on the value of the process at the last moment of those which appear in the condition. Therefore, the Markov process can also be called a process without after-effects.

By virtue of (2.3.6), for a Markov process formula (2.3.5) takes the form

$$\begin{aligned} w(y(t_1), \dots, y(t_n)) &= w(y(t_1)) w(y(t_2)|y(t_1)) \\ &\times w(y(t_3)|y(t_2)) \dots w(y(t_n)|y(t_{n-1})) \end{aligned} \quad (2.3.7)$$

for $t_n > t_{n-1} > \dots > t_1$.

We see that for a Markov process, the many-time probability densities of arbitrary multiplicity n are determined by the one-time probability density $w(y(t))$ and by the two-time conditional probability density $w(y(t)|y(t'))$, $t > t'$, which is called the transition probability density or, for short, transition probability.

2.3.2 The Smoluchowski–Chapman Equation and Its Consequences

Let us integrate the three-time probability density $w(y(t_3), y(t_2), y(t_1))$ with respect to $y(t_2)$ from $-\infty$ to ∞ . We then obtain the two-time probability density

$$\int w(y(t_1), y(t_2), y(t_3)) dy(t_2) = w(y(t_1), y(t_3)). \quad (2.3.8)$$

Now let us represent both probability densities in the form (2.3.7). Dropping $w(y(t_1))$, we obtain the equation

$$\int w(y(t_3)|y(t_2)) w(y(t_2)|y(t_1)) dy(t_2) = w(y(t_3)|y(t_1)) \quad (t_1 < t_2 < t_3), \quad (2.3.9)$$

which is called the Smoluchowski–Chapman equation. The transition probabilities must satisfy this equation.

Denoting $y(t_1) = y''$, $y(t_2) = y'$, we can write the transition probability density $w(y(t_2)|y(t_1))$ in the form $w_{t_2 t_1}(y'|y'')$. Here we explicitly show that it is a function of the times t_1 and t_2 . Then (2.3.9) can be rewritten in the form

$$\int w_{t_3 t_2}(y|y') w_{t_2 t_1}(y'|y'') dy' = w_{t_3 t_1}(y|y''), \quad (2.3.10)$$

where $y = y(t_3)$, $y' = y(t_2)$, $y'' = y(t_1)$.

Let us introduce the conditional characteristic function

$$\Theta_{t_3 t_2}(iu|y') = \int \exp(iu \Delta y) w_{t_3 t_2}(y|y') dy \quad (2.3.11)$$

of increments $\Delta y = y - y' = y(t_3) - y(t_2)$. Here $u \Delta y = \sum_{\alpha=1}^r u_\alpha \Delta y_\alpha$. This is the Fourier transform of $w_{t_3 t_2}(y|y')$. Using the inverse transformation one can express the transition probability density $w_{t_3 t_2}(y|y')$ in terms of the characteristic function

$$w_{t_3 t_2}(y|y') = (2\pi)^{-r} \int \exp[-iu(y - y')] \Theta_{t_3 t_2}(iu|y') du. \quad (2.3.12)$$

Inserting (2.3.12) into (2.3.10), we find

$$(2\pi)^{-r} \int \Theta_{t_3 t_2}(iu|y') \exp[-iu(y - y')] w_{t_2 t_1}(y'|y'') du dy' = w_{t_3 t_1}(y|y''). \quad (2.3.13)$$

One can easily see that the last equation may be written as

$$(2\pi)^{-r} \int \Theta_{t_3 t_2}(-\partial/\partial y|y') \exp[-iu(y - y')] w_{t_2 t_1}(y'|y'') du dy' = w_{t_3 t_1}(y|y''). \quad (2.3.14)$$

First of all let us integrate this equation with respect to u by using the formula

$$(2\pi)^{-r} \int_{-\infty}^{\infty} e^{iuz} du = \delta(z) \equiv \delta(z_1) \dots \delta(z_r), \quad (2.3.15)$$

which is the well-known integral representation of the delta function. Hence, we have

$$\int \Theta_{t_3 t_2}(-\partial/\partial y|y') \delta(y - y') w_{t_2 t_1}(y'|y'') dy' = w_{t_3 t_1}(y|y''). \quad (2.3.16)$$

Because of the properties of the delta function, the integration with respect to y' is trivial. It gives

$$N_{\partial, y} \Theta_{t_3 t_2} \left(-\frac{\partial}{\partial y} \Big| y \right) w_{t_2 t_1}(y|y'') = w_{t_3 t_1}(y|y''). \quad (2.3.17)$$

Here we have inserted the symbol $N_{\partial, y}$, which indicates that the differentiation is done last, i.e. the operators $\partial/\partial y_\alpha$ appear on the left and act only when the multiplication by the functions of y has been carried out on the right.

Equation (2.3.17) is quite equivalent to the Smoluchowski–Chapman equation (2.3.10). If we use formula (2.1.4), which gives the representation of the characteristic function in the form of an expansion, we obtain the following form of the Smoluchowski–Chapman equation:

$$\begin{aligned} w_{t_3 t_1}(y|y'') &= w_{t_2 t_1}(y|y'') + \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \\ &\times \sum_{\alpha_1, \dots, \alpha_m=1}^r \frac{\partial^m}{\partial y_{\alpha_1} \dots \partial y_{\alpha_m}} [\langle \Delta y_{\alpha_1} \dots \Delta y_{\alpha_m} \rangle_y w_{t_2 t_1}(y|y'')] . \end{aligned} \quad (2.3.18)$$

Here the subscript y shows that the moments are conditional, i.e. they are taken at fixed values of $y = y(t_2)$.

2.3.3 The Master Equation

We write (2.3.17) in the form

$$\begin{aligned} \tau^{-1}[w_{t_3 t_1}(y|y'') - w_{t_2 t_1}(y|y'')] \\ = \tau^{-1} \left[N_{\partial, y} \Theta_{t_3 t_2} \left(-\frac{\partial}{\partial y} \Big| y \right) - 1 \right] w_{t_2 t_1}(y|y'') , \end{aligned} \quad (2.3.19)$$

where $\tau = t_3 - t_2 > 0$. Now, let τ tend to zero. Assuming that the limit

$$\Phi_{t_2}(v, y) = \lim_{\tau \rightarrow 0} \tau^{-1} [\Theta_{t_2 + \tau, t_2}(v|y) - 1] \quad (2.3.20)$$

exists, we obtain from (2.3.19) the equation

$$\frac{\partial}{\partial t_2} w_{t_2 t_1}(y|y'') = N_{\partial, y} \Phi_{t_2} \left(-\frac{\partial}{\partial y}, y \right) w_{t_2 t_1}(y|y'') \quad (2.3.21)$$

which is called the master equation. The “initial” condition for (2.3.21) has the form

$$w_{t_2 t_1}(y|y'') = \delta(y - y'') \quad \text{for } t_2 = t_1 . \quad (2.3.22)$$

If the function $\Phi_t(v, y)$ is known, one can find the transition probabilities as the solution of (2.3.21) with the “initial” condition (2.3.22). In this sense the Markov operator $L_t = N_{\partial, y} \Phi_t(-\partial/\partial y, y)$ defines the statistics of the Markov process.

If (2.3.21) is multiplied by $w_{t_1}(y'') = w(y(t_1))$ and the product is integrated with respect to $y'' = y(t_1)$, we find that the one-time probability density $w_t(y) = \int w_{tt_1}(y|y'') w_{t_1}(y'') dy''$ satisfies the analogous equation

$$\frac{\partial w_t(y)}{\partial t} = N_{\partial, y} \Phi_t \left(-\frac{\partial}{\partial y}, y \right) w_t(y) . \quad (2.3.23)$$

It is also called the master equation.

The above-considered process of taking the limit $\tau \rightarrow 0$ can also be carried out in (2.3.18). The master equation (2.3.23) will then be of the form

$$\frac{\partial w_t(y)}{\partial t} = \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \sum_{\alpha_1, \dots, \alpha_m=1}^r \frac{\partial^m}{\partial y_{\alpha_1} \dots \partial y_{\alpha_m}} [K_{\alpha_1 \dots \alpha_m}(y) w_t(y)] , \quad (2.3.24)$$

where

$$K_{\alpha_1 \dots \alpha_m}(y) = \lim_{\tau \rightarrow 0} [\tau^{-1} \langle \Delta y_{\alpha_1} \dots \Delta y_{\alpha_m} \rangle_y] . \quad (2.3.25)$$

The function (2.3.20) and the coefficients (2.3.25) are related by

$$\Phi(v, y) = \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{\alpha_1, \dots, \alpha_m} K_{\alpha_1 \dots \alpha_m}(y) v_{\alpha_1} \dots v_{\alpha_m} . \quad (2.3.26)$$

The series is assumed to be convergent. Equation (2.3.24) is called the Kramers–Moyal equation.

2.3.4 The Fokker–Planck Equation and Its Invariant Form

The functions (2.3.25) will be called the coefficients of the master equation or the coefficient functions. The master equation (2.3.24) is called the Fokker–Planck equation when the only nonzero coefficients are $K_\alpha(y)$ and $K_{\alpha\beta}(y)$. It then has the form

$$\frac{\partial w(y)}{\partial t} = - \frac{\partial}{\partial y_\alpha} [K_\alpha(y) w(y)] + \frac{1}{2} \frac{\partial^2}{\partial y_\alpha \partial y_\beta} [K_{\alpha\beta}(y) w(y)] . \quad (2.3.27)$$

Here and in all subsequent sections summation over repeated subscripts is understood. The transition probabilities $w_{t_2 t_1}(y|y'')$ satisfy the same equation.

Note that for non-Euclidean space with the metric tensor $g_{\alpha\beta}$ (which is independent of time) the Fokker–Planck equation (2.3.27) can be written in a form that is invariant under arbitrary curvilinear transformations. Namely,

$$g^{-1/2} \frac{\partial w}{\partial t} = - (G^\alpha)_{;\alpha} . \quad (2.3.28)$$

Here $(\dots)_{;\alpha}$ denotes the covariant derivative; $g = \det \|g_{\alpha\beta}\| > 0$; $g^{-1/2}(y) w(y)$ is a scalar; G^α is a contravariant vector defined by

$$G^\alpha = D^\alpha g^{-1/2} w - \frac{1}{2} (E^{\alpha\beta} g^{-1/2} w)_{;\beta} . \quad (2.3.29)$$

In the last formula we have designated

$$E^{\alpha\beta} = K^{\alpha\beta}, \quad D^\alpha = K^\alpha + \frac{1}{2} \Gamma_{\beta\gamma}^\alpha K^{\beta\gamma} , \quad (2.3.30)$$

where K^α and $K^{\alpha\beta}$ are the coefficient functions from (2.3.27) [the vector $y = (y^\alpha)$ is assumed to be contravariant]; $\Gamma_{\beta\gamma}^\alpha$ are the Christoffel symbols [2.2–4]. Using the formulas of transformations of the functions K^α and $K^{\alpha\beta}$ when variables transform as $y' = f(y)$ and also applying the formula of the transformations of the Christoffel symbols

$$\Gamma'^\sigma_{\rho\tau} = \Gamma^\alpha_{\beta\gamma} \frac{\partial y'^\sigma}{\partial y^\alpha} \frac{\partial y^\beta}{\partial y'^\rho} \frac{\partial y^\gamma}{\partial y'^\tau} + \frac{\partial^2 y^\alpha}{\partial y'^\rho \partial y'^\tau} \frac{\partial y'^\sigma}{\partial y^\alpha} , \quad (2.3.31)$$

we easily verify that D^α and $E^{\alpha\beta}$ are the contravariant vector and tensor, respectively.

Let us show that the covariant equation (2.3.28) is equivalent to (2.3.27). According to the well-known formula of tensor calculus [2.2, 3],

$$(A^{\alpha\beta})_{;\beta} = g^{-1/2} \partial(g^{1/2} A^{\alpha\beta})/\partial y^\beta + \Gamma_{\beta\sigma}^\alpha A^{\sigma\beta}. \quad (2.3.32)$$

Therefore, putting here $A^{\alpha\beta} = E^{\alpha\beta} w g^{-1/2}$ from (2.3.29) we have

$$\begin{aligned} G^\alpha &= g^{-1/2} [D^\alpha w - 1/2 \partial(E^{\alpha\beta} w)/\partial y^\beta - 1/2 \Gamma_{\beta\sigma}^\alpha E^{\sigma\beta} w] \\ &= g^{-1/2} [K^\alpha w - 1/2 \partial(K^{\alpha\beta} w)/\partial y^\beta], \end{aligned} \quad (2.3.33)$$

where (2.3.30) is used. Substituting (2.3.33) into (2.3.28) and applying another formula of tensor calculus [2.2, 3], namely, $A_{;\alpha}^\alpha = g^{-1/2} \partial(g^{1/2} A^\alpha)/\partial y^\alpha$, we obtain (2.3.27).

From (2.3.28, 29) we see that the corresponding master equation has the form

$$\frac{\partial w}{\partial t} = g^{1/2} L_0 g^{-1/2} w, \quad (2.3.34)$$

where L_0 is an invariant operator.

The master equation has the invariant form (2.3.34) not just in the case of the Fokker–Planck equation. Let us take, for instance, the equation

$$\frac{\partial w}{\partial t} = -\frac{\partial}{\partial y^\alpha}(K^\alpha w) + \frac{1}{2} \frac{\partial^2}{\partial y^\alpha \partial y^\beta}(K^{\alpha\beta} w) - \frac{1}{6} \frac{\partial^3}{\partial y^\alpha \partial y^\beta \partial y^\gamma}(K^{\alpha\beta\gamma} w) \quad (2.3.35)$$

(as is well known, the nonnegativity of $w(y)$ is slightly violated for this equation, but it is now of no importance). In the last equation, instead of (2.3.29), we must put

$$G^\alpha = D^\alpha g^{-1/2} w - \frac{1}{2} (E^{\alpha\beta} g^{-1/2} w)_{;\beta} + \frac{1}{6} ((F^{\alpha\beta\gamma} g^{-1/2} w)_{;\gamma})_{;\beta}, \quad (2.3.36)$$

where D^α , $E^{\alpha\beta}$ and $F^{\alpha\beta\gamma}$ are contravariant tensors, which are defined by

$$\begin{aligned} F^{\alpha\beta\gamma} &= K^{\alpha\beta\gamma}, \\ E^{\alpha\beta} &= K^{\alpha\beta} + \frac{1}{2} (\Gamma_{\gamma\delta}^\alpha K^{\beta\gamma\delta} + \Gamma_{\gamma\delta}^\beta K^{\alpha\gamma\delta}), \\ D^\alpha &= K^\alpha + \frac{1}{2} \Gamma_{\beta\gamma}^\alpha K^{\beta\gamma} + \frac{1}{6} \left(\Gamma_{\beta\sigma}^\alpha \Gamma_{\gamma\delta}^\sigma + \frac{\partial \Gamma_{\gamma\delta}^\alpha}{\partial y^\beta} \right) K^{\beta\gamma\delta}. \end{aligned} \quad (2.3.37)$$

These equations can be proved by means of the same line of reasoning as (2.3.29, 30).

Equation (2.3.34) is also valid in this case. If other coefficient functions $K^{\alpha\cdots\omega}$ are also considered, then additional terms appear on the right-hand sides of (2.3.36, 37).

2.3.5 The Stationary Markov Process

A random process is called stationary if all many-time probability densities

$$w(y(t_1), \dots, y(t_n)) \quad (2.3.38)$$

are constant in time, i.e. if the substitution $t_1 + a, \dots, t_n + a$ for t_1, \dots, t_n leaves them unchanged. In this case the functions (2.3.38) depend only on $(n - 1)$ time

differences, for example, on $t_2 - t_1 = t_{21}, \dots, t_n - t_1 = t_{n1}$. Considering (2.3.7), we see that for the Markov process the condition of stationarity reduces to the following two requirements.

1. The one-time probability density $w(y(t))$ must not depend on t .
2. The transition probabilities $w_{tt'}(y|y')$ must depend only on the time difference $\tau = t - t'$.

It is easy to see that in the stationary case the characteristic function (2.3.11) must depend only on the time difference $t_3 - t_2$, and the function (2.3.20) must not depend on time t . In the stationary case, (2.3.21) is of the form

$$\partial w_\tau(y|y')/\partial\tau = N_{\partial,y}\Phi(-\partial/\partial y, y)w_\tau(y|y''). \quad (2.3.39)$$

The last equation and the initial condition

$$w_\tau(y|y'') = \delta(y - y'') \quad \text{for } \tau = 0 \quad (2.3.40)$$

completely determine the transition probabilities $w_\tau(y|y'')$. Equation (2.3.23) written for the one-time stationary probability density $w_{st}(y)$ has the form

$$N_{\partial,y}\Phi(-\partial/\partial y, y)w_{st}(y) = 0 \quad (2.3.41)$$

since $w_{st}(y)$ is constant in time. This equation and the normalization condition

$$\int w(y) dy = 1 \quad (2.3.42)$$

completely determine the stationary one-time probability density. Thus, we see that the operator of the master equation, i.e. the function $\Phi(v, y)$, completely determines the statistical properties of the stationary Markov process.

2.4 Infinitely Divisible Probability Densities and Markov Processes

2.4.1 Infinitely Divisible Probability Density

The probability density $w(\xi)$ of a random variable ξ is called infinitely divisible if this variable can be represented as the sum $\eta_1 + \eta_2 + \dots + \eta_n$ of any large number n of independent random variables η_j having the same probability densities $w_n(\eta)$. We introduce the corresponding characteristic functions

$$\Theta(iu) = \int e^{iu\xi} w(\xi) d\xi, \quad (2.4.1)$$

$$\Theta_n(iu) = \int e^{iun} w_n(\eta) d\eta. \quad (2.4.2)$$

As is well known, the characteristic function of the sum of statistically independent random variables is the product of the characteristic functions of the individual

variables. In the present case, since the summands have the same probability densities and the same characteristic functions, the characteristic function of the sum is equal to the power of the characteristic function $\Theta_n(iu)$, i.e.

$$\Theta(iu) = [\Theta_n(iu)]^n . \quad (2.4.3)$$

By virtue of (2.4.3) the condition of infinite divisibility of the probability density $w(\xi)$ reduces to the fact that the expression $[\Theta(iu)]^{1/n}$ must be a characteristic function of a random variable. This means that the function

$$w_n(\eta) = (2\pi)^{-1} \int e^{-iu\eta} [\Theta(iu)]^{1/n} du , \quad (2.4.4)$$

which is obtained by inverse Fourier transformation of (2.4.2), must have the properties of a probability density, i.e. it must be nonnegative and normalized. The normalization property follows from the normalization of the probability density $w(\xi)$, in other words, from $\Theta(0) = 1$. In fact, from (2.4.4) we have

$$\int w_n(\eta) d\eta = \int du [(2\pi)^{-1} \int d\eta e^{-iu\eta}] [\Theta(iu)]^{1/n} = \int \delta(u) [\Theta(iu)]^{1/n} du , \quad (2.4.5)$$

i.e.

$$\int w_n(\eta) d\eta = [\Theta(0)]^{1/n} = 1 . \quad (2.4.6)$$

We now consider the property of nonnegativity. Thus, the probability density is infinitely divisible if the corresponding characteristic function satisfies the inequality

$$\int e^{-iu\eta} [\Theta(iu)]^{1/n} d\eta \geq 0 \quad (2.4.7)$$

for any n and η . For infinitely divisible probability density (for one-component variable ξ) the following theorem is well known (see, for example, [2.5]):

The probability density $w(\xi)$ satisfying the condition

$$\int \xi^2 w(\xi) d\xi < \infty \quad (2.4.8)$$

is infinitely divisible if and only if the following integral representation is valid:

$$\ln \Theta(iu) = i\gamma u + \int_{-\infty}^{\infty} [e^{iz} - 1 - iz] z^{-2} g(z) dz . \quad (2.4.9)$$

Here γ is a real constant; $g(z)$ is a function with the properties

$$g(z) \geq 0 , \quad (2.4.10a)$$

$$\int_{-\infty}^{\infty} g(z) dz < \infty . \quad (2.4.10b)$$

Here the function $g(z)$ can have the singularities of the type of the delta function.

Representation (2.4.9) is called the canonical representation. The condition (2.4.8) can be omitted if in (2.4.9) the expression $[\exp(iuz) - 1 - iuz]$ is replaced by $[\exp(iuz) - 1 - iu \sin z]$ (in doing so (2.4.10b) drops out). But after this replacement, the function $g(z)$ loses its scalar property with respect to linear transformations $u \rightarrow \lambda u$, $z \rightarrow \lambda^{-1} z$. We therefore choose the form of representation given by (2.4.9). This form is also more convenient for covariant many-component generalization.

The results obtained for one random variable can be generalized to the case of several random variables $\xi = (\xi_1, \dots, \xi_n)$. The difference between the two cases consists in the fact that η , u and $z = (z_1, \dots, z_r)$ are vectors when ξ is vector. In (2.4.9) dz means $dz_1 \dots dz_r$, and uz and z^2 mean $\sum u_\alpha z_\alpha$ and $\sum z_\alpha^2$, respectively. The condition (2.4.8) must certainly be replaced by

$$\sum_{\alpha} \int \xi_{\alpha}^2 w(\xi) d\xi < \infty . \quad (2.4.11)$$

We shall not give a rigorous proof of the validity of the expansion (2.4.9) in the many-variable case. However, some considerations concerning this problem are given in Appendix 2.

2.4.2 Stationary Markov Process with Independent Increments

Let us consider a stationary process $y(t) = (y_1(t), \dots, y_r(t))$. It is a process with independent increments if the increments $y(t_2) - y(t_1)$, $y(t_3) - y(t_2)$, \dots , $y(t_m) - y(t_{m-1})$ are statistically independent for any moments t_1, t_2, \dots, t_n satisfying the inequality $t_1 < t_2 < \dots < t_n$.

It is easy to understand that for a stationary process with independent increments the probability density $w(y(t_2) - y(t_1))$ is infinitely divisible for $t_2 > t_1$. In fact, the increment can be represented in the form

$$\begin{aligned} y(t_2) - y(t_1) = & [y(t_1 + \Delta) - y(t_1)] + [y(t_1 + 2\Delta) \\ & - y(t_1 + \Delta)] + \dots + [y(t_2) - y(t_2 - \Delta)] , \end{aligned} \quad (2.4.12)$$

where $\Delta = (t_2 - t_1)/n$; n is arbitrary.

All the summands on the right-hand side of (2.4.12) are independent because $y(t)$ is a process with independent increments; they have the same probability densities due to the stationarity of the process. Therefore, if $[y(t + \tau) + y(t)]^2 < \infty$, the characteristic function

$$\Theta_{\tau}(iu) = \langle \exp\{iu[y(t + \tau) - y(t)]\} \rangle \quad (2.4.13)$$

can be represented in the form (2.4.9):

$$\ln \Theta_{\tau}(iu) = i\gamma_{\tau} u + \int (e^{iuz} - 1 - iuz) z^{-2} g_{\tau}(z) dz , \quad (2.4.14)$$

where $g_{\tau}(z)$ satisfies the conditions (2.4.10).

From the condition of the independence of the increments we find that the characteristic function $\Theta_\tau(iu)$ satisfies the equation

$$\Theta_{\tau_1 + \tau_2}(iu) = \Theta_{\tau_1}(iu) \Theta_{\tau_2}(iu). \quad (2.4.15)$$

This implies that $\ln \Theta_\tau(iu)$ is proportional to τ :

$$\ln \Theta_\tau(iu) = \tau \varphi(iu). \quad (2.4.16)$$

Comparing (2.4.16) with (2.4.14), we easily see that γ_τ and $g_\tau(z)$ must be proportional to τ :

$$\gamma_\tau = \gamma_1 \tau, \quad g_\tau(z) = g_1(z) \tau. \quad (2.4.17)$$

The process with independent increments is a Markov process. In fact, let us consider the increments

$$\begin{aligned} \Delta_k &= y(t_k) - y(t_{k-1}); \quad \Delta_{k-1} = y(t_{k-1}) - y(t_{k-2}); \dots; \quad \Delta_2 = y(t_2) - y(t_1) \\ (t_k > t_{k-1} > \dots > t_1). \end{aligned} \quad (2.4.18)$$

We have

$$\begin{aligned} y(t_k) &= y(t_{k-1}) + \Delta_k; \quad y(t_{k-2}) = y(t_{k-1}) - \Delta_{k-1}; \\ y(t_{k-3}) &= y(t_{k-1}) - \Delta_{k-1} - \Delta_{k-2}; \dots; \quad y(t_1) = y(t_{k-1}) - \Delta_{k-1} - \dots - \Delta_2. \end{aligned} \quad (2.4.19)$$

Consequently, the conditional probability density $w(y(t_k)|y(t_{k-1}))$ is determined by the probability density $w(\Delta_k)$. Let us add the condition of fixed $y(t_{k-2})$ to the condition of fixed $y(t_{k-1})$; the former fixes the increment Δ_{k-1} by virtue of the second equation (2.4.19). However, Δ_k and Δ_{k-1} are independent. Therefore, if we know Δ_{k-1} , we cannot have a more precise knowledge of Δ_k and, consequently, of $y(t_k)$. In other words, according to (2.4.19), the equation

$$w(\Delta_k|\Delta_{k-1}) = w(\Delta_k) \quad (2.4.20)$$

implies

$$w(y(t_k)|y(t_{k-1}), y(t_{k-2})) = w(y(t_k)|y(t_{k-1})). \quad (2.4.21)$$

The same thing can be said about the other increments. As a consequence of (2.4.19), the equation

$$w(\Delta_k|\Delta_{k-1}, \dots, \Delta_2) = w(\Delta_k) \quad (2.4.22)$$

implies the formula (2.3.6), which is the definition of a Markov process. However, for independent increments the characteristic function (2.3.11) loses the dependence on y' unlike the general case of the Markov process.

Now we proceed to the master equation (2.3.21). Using (2.4.16), from (2.3.20) we have, after passing to the limit,

$$\Phi(v) = \varphi(v), \quad (2.4.23)$$

so that the master equation (2.3.21) takes the form

$$\partial w_\tau(y|y'')/\partial \tau = \varphi(-\partial/\partial y) w_\tau(y|y''). \quad (2.4.24)$$

In so doing, by virtue of (2.4.14, 16, 17) the function $\Phi(v)$ can be written as

$$\Phi(v) = \varphi(v) = K_\alpha v_\alpha + \int_{-\infty}^{\infty} (e^{vz} - 1 - vz) z^{-2} g_1(z) dz, \quad \operatorname{Re}\{v\} = 0. \quad (2.4.25)$$

Here we have substituted K_α for $\gamma_{1\alpha}$. Comparing (2.4.25) with (2.3.26) we see that this can be done. According to (2.4.10, 17), the function $g_1(z)$ in (2.4.25) must satisfy the analogous conditions:

$$g_1(z) \geq 0, \quad \int_{-\infty}^{\infty} g_1(z) dz \leq \infty. \quad (2.4.26)$$

If conditions (2.4.25, 26) were violated, some of the probability densities related to the process $y(t)$ would lose their nonnegativity.

2.4.3 Arbitrary Markov Processes

Let us return to the general stationary Markov process. Strictly speaking, in this case the probability densities of increments $y(t_2) - y(t_1)$ are not infinitely divisible, but we can say that they are approximately infinitely divisible for small $\tau = t_2 - t_1$.

Let us fix the moment of time t_1 and let $t_2 = t_1 + \tau$ vary. The characteristic function $\Theta_\tau(iu|y'')$ defined by (2.3.11) corresponds to the probability density $w_\tau(y|y'') = w_{t_2 t_1}(y|y'')$. Fixing a value τ_0 , we build the family of functions

$$\Theta'_\tau(iu|y'') = [\Theta_{\tau_0}(iu|y'')]^{\tau/\tau_0}. \quad (2.4.27)$$

These functions and the family of functions $w'_\tau(y|y'')$ are related by a formula of the type (2.3.11). Writing the inverse transformation, we have

$$w'_\tau(y|y'') = (2\pi)^{-r} \int_{-\infty}^{\infty} \exp[-iu(y - y'')] [\Theta_{\tau_0}(iu|y'')]^{\tau/\tau_0} du. \quad (2.4.28)$$

Since the probability density $w_{\tau_0}(y|y'')$ must not necessarily be infinitely divisible, the function (2.4.28) is not necessarily required to be the probability density at $\tau_0/\tau = n$, and, moreover, it is not required to be nonnegative for other τ except at $\tau = \tau_0, 2\tau_0, 3\tau_0, \dots$. At these values it must be nonnegative since the probability density of random variables $y(t_1 + \tau_0) - y(t_1)$ and the probability density of the sum of an arbitrary number of independent random variables with identical probability densities is nonnegative. It may be recalled that the composition of probability densities is the probability density.

Passing to the limit $\tau_0 \rightarrow 0$ in (2.4.27, 28), we consider the functions

$$\tilde{\Theta}_\tau(iu|y'') = \lim_{\tau_0 \rightarrow 0} [\Theta_{\tau_0}(iu|y'')]^{\tau/\tau_0}, \quad (2.4.29)$$

$$\tilde{w}_\tau(y|y'') = (2\pi)^{-r} \int_{-\infty}^{\infty} \exp[-iu(y - y'')] \tilde{\Theta}_\tau(iu|y'') du. \quad (2.4.30)$$

We assume that the limit in (2.4.29, 30) exists.

If the function (2.4.30) is continuous with respect to τ , it must be nonnegative for any value of τ . In fact, the points $\tau = m\tau_0$ (m is a natural number) will be positioned

more and more compactly on the halfline $\tau > 0$ as we approach the limit $\tau_0 \rightarrow 0$. Hence, for an arbitrary fixed $\tau = \tau' > 0$ in (2.4.28) the distance from τ' to the nearest point of a set $m\tau_0$ (where the function $w'_\tau(y|y'')$ is nonnegative) will tend to zero for $\tau_0 \rightarrow 0$. Consequently, $\tilde{w}_\tau(y|y'')$ is nonnegative for any $\tau = \tau'$ due to its continuity.

The nonnegativity which we have just proved for the function (2.4.30) implies that $\tilde{w}_\tau(y|y'')$ is an infinitely divisible probability density and that the probability densities (2.4.30) can be treated as the transition probabilities of a stationary process $\tilde{y}(t)$ with independent increments. In fact, we easily see that the functions (2.4.29) satisfy the condition (2.4.15). The process $\tilde{y}(t)$ with independent increments can be called “tangent” at a point t_1 with respect to the initial Markov process $y(t)$.

Substituting (2.4.29) into (2.4.16), we find the function (2.4.23) corresponding to the process $\tilde{y}(t)$. We get

$$\tilde{\varphi}(iu) = \lim_{\tau_0 \rightarrow 0} \tau_0^{-1} \ln \Theta_{\tau_0}(iu|y'') . \quad (2.4.31)$$

But the limit (2.4.31) coincides with the limit (2.3.20), so that

$$\tilde{\varphi}(iu) = \Phi(iu, y'') . \quad (2.4.32)$$

The formulas (2.4.25, 26) are valid for the process $\tilde{y}(t)$ as for every process with independent increments. Using (2.4.32), we can write these formulas in the form

$$\Phi(iu, y'') = K_\alpha(y'') iu_\alpha + \int_{-\infty}^{\infty} (e^{iuz} - 1 - iuz) z^{-2} g(z, y'') dz , \quad (2.4.33)$$

where

$$g(z, y'') \geq 0, \quad \int g(z, y'') dz < \infty . \quad (2.4.34)$$

The results obtained can be summarized in the following way: if there is a Markov process such that the limit (2.4.30) exists and the function $\tilde{w}_\tau(y|y'')$ is continuous in τ and satisfies the condition

$$\int \sum_\alpha y_\alpha^2 \tilde{w}_\tau(y|y'') dy < \infty , \quad (2.4.35)$$

then the corresponding function $\Phi(iu, y)$, which determines the Markov operator, can be represented in the form (2.4.33) with (2.3.34) being valid. The inverse statement is also justified: any function satisfying the condition (2.4.34) determines the Markov process for which (2.4.33, 35) are valid.

2.5 Notes on References to Chapter 2

A treatment of correlators or cumulants is given, for example, in [2.6, 7]. Concepts and fundamental principles of equilibrium statistical thermodynamics can be found in many texts including [2.8–10]. The case of an arbitrary number of the pairs of

conjugate thermodynamic parameters denoted by A_i, a_i is considered in [2.9]; our designation of thermodynamic parameters is borrowed from this work. The treatment of the subject of Sect. 2.2 is similar to the one given in [2.1].

The foundations of the theory of Markov processes can also be found in many texts including [2.7, 11].

Infinitely divisible probability densities are described in [2.5, 12].

3. The Generating Equation of Markov Nonlinear Nonequilibrium Thermodynamics

In this chapter the kinetic potential and its image are introduced and their properties are investigated. The knowledge of kinetic potential or of its image is equivalent to the knowledge of the Markov operator. Hence, each of these functions describes all statistical properties of fluctuating internal parameters.

Concepts of kinetic potential and its image are useful since the most fundamental equation of the Markov nonequilibrium thermodynamics, namely, the generating equation is conveniently written in terms of them. The generating equation is based on the principle of time reversibility and on the principle of dynamic equilibrium. The latter principle signifies the validity of the formulas that express the one-time equilibrium probability density of internal parameters in terms of energy or entropy. If the condition of time reversibility is not fulfilled, the more special generating equation based only on the dynamic equilibrium principle is valid.

The explicit form of the kinetic potential and of its image will be found for some examples: for the model of nonlinear resistance, for chemical reactions and for the diffusion process. The validity of the generating equation is demonstrated. The paradox connected with detection of thermal fluctuations will be discussed for the nonlinear resistance model.

3.1 Kinetic Potential

3.1.1 Definition of Kinetic Potential

According to (2.2.30) the double, triple, etc., equilibrium correlators of internal thermodynamic parameters are macroscopically small quantities. The reason is that the Boltzmann constant is small macroscopically, and the temperature T and the free energy $F(a)$ are macroscopic in nature. Hence, the temperature T and the derivatives of free energy with respect to a have zero order in the small parameter k , i.e. they are not very large or very small. The Boltzmann constant can be regarded as a basic small parameter of the theory. Of course, k is not dimensionless, but multiplying k by a quantity having appropriate dimensions, we can obtain dimensionless small parameter of the order of k .

If we proceed from one-time equilibrium correlators to many-time correlators $\langle B_{\alpha_1}(t_1), B_{\alpha_2}(t_2), \dots, B_{\alpha_m}(t_m) \rangle$, $m \geq 2$ and to conditional correlators of increments

$$\langle B_{\alpha_1}(t_2) - B_{\alpha_1}(t_1), \dots, B_{\alpha_m}(t_2) - B_{\alpha_m}(t_1) \rangle_{B(t_1)},$$

it is natural to suppose that all of them are as small as the one-time equilibrium correlators both in the Markov and non-Markov cases, i.e. for a given m they have the same order in k :

$$\langle B_{\alpha_1}(t_2) - B_{\alpha_1}(t_1), \dots, B_{\alpha_m}(t_2) - B_{\alpha_m}(t_1) \rangle_{B(t_1)} \sim k^{m-1} \quad (3.1.1)$$

by analogy with (2.2.30).

We shall regard the equilibrium fluctuations $B(t) = (B_1(t), \dots, B_r(t))$ of internal thermodynamic parameters as the stationary Markov process. This process is characterized by the coefficients (2.3.25) of the master equation (2.3.24), i.e. by coefficients

$$K_{\alpha_1 \dots \alpha_m}(B) = \lim_{\tau \rightarrow 0} [\tau^{-1} \langle \Delta B_{\alpha_1} \dots \Delta B_{\alpha_m} \rangle_B], \quad (3.1.2)$$

where $\Delta B = B(t_1 + \tau) - B(t_1)$, $B = B(t_1)$.

We assume that the limit on the right-hand side of (3.1.2) exists. From (3.1.2) we obtain the following estimation formulas for small $\tau > 0$:

$$\langle \Delta B_{\alpha_1} \dots \Delta B_{\alpha_m} \rangle_B = K_{\alpha_1 \dots \alpha_m}(B) \tau + o(\tau). \quad (3.1.3)$$

Let us use the formulas

$$\begin{aligned} \langle \Delta B_{\alpha_1}, \Delta B_{\alpha_2} \rangle_B &= \langle \Delta B_{\alpha_1} \Delta B_{\alpha_2} \rangle_B - \langle \Delta B_{\alpha_1} \rangle_B \langle \Delta B_{\alpha_2} \rangle_B, \\ \langle \Delta B_{\alpha_1}, \Delta B_{\alpha_2}, \Delta B_{\alpha_3} \rangle_B &= \langle \Delta B_{\alpha_1} \Delta B_{\alpha_2} \Delta B_{\alpha_3} \rangle_B - (3) \langle \Delta B_{\alpha_1} \Delta B_{\alpha_2} \rangle_B \langle \Delta B_{\alpha_3} \rangle_B \\ &\quad + 2 \langle \Delta B_{\alpha_1} \rangle_B \langle \Delta B_{\alpha_2} \rangle_B \langle \Delta B_{\alpha_3} \rangle_B, \end{aligned} \quad (3.1.4)$$

etc., which are the inverse of the formulas (2.1.12–15). Inserting (3.1.3) into them, we get

$$\langle \Delta B_{\alpha_1}, \dots, \Delta B_{\alpha_m} \rangle_B = K_{\alpha_1 \dots \alpha_m}(B) \tau + o(\tau). \quad (3.1.5)$$

Hence, the coefficients of the master equation can be determined not only in terms of moments, but also in terms of correlators

$$K_{\alpha_1 \dots \alpha_m}(B) = \lim_{\tau \rightarrow 0} [\tau^{-1} \langle \Delta B_{\alpha_1}, \dots, \Delta B_{\alpha_m} \rangle_B]. \quad (3.1.6)$$

Now we take into account the estimation (3.1.1) of the correlator on the right-hand side of (3.1.6). We obtain that the coefficients (3.1.6) are small for $m \geq 2$ and progressively decrease with the increase of m :

$$K_{\alpha_1 \dots \alpha_m}(B) \sim k^{m-1}, \quad m \geq 1. \quad (3.1.7)$$

We see that the coefficients of the master equation and one-time equilibrium correlators have identical orders of magnitude. For them we write the formulas

$$K_{\alpha_1 \dots \alpha_m}(B) = (kT)^{m-1} \left[\frac{\partial^m V(y, B)}{\partial y_{\alpha_1} \dots \partial y_{\alpha_m}} \right]_{y=0}, \quad m \geq 1, \quad (3.1.8)$$

which are to some extent analogous to (2.2.30). The formulas (3.1.8) define the nonequilibrium kinetic potential $V(y, B)$, which has a macroscopic nature just like the free energy in (2.2.30). This means that the potential $V(y, B)$ and its derivatives

with respect to y or B are zeroth order in k , i.e. they do not include k other than in product with some large parameter.

Considering (3.1.8), we can write the kinetic potential in the form of its Taylor expansion:

$$V(y, B) = \sum_{m=1}^{\infty} \frac{1}{m!} \beta^{m-1} \sum_{\alpha_1, \dots, \alpha_m} K_{\alpha_1 \dots \alpha_m}(B) y_{\alpha_1} \dots y_{\alpha_m} \quad (3.1.9)$$

($\beta^{-1} = kT$). Comparing (3.1.9) with the expansion (2.3.26), we obtain the relation between the kinetic potential and the function (2.3.20), which is not macroscopic in nature unlike the kinetic potential. This relation has the form

$$\Phi(v, B) = \beta V(kTv, B). \quad (3.1.10)$$

By virtue of (3.1.10) the master equation (2.3.23) can be written as

$$\frac{\partial w(B)}{\partial t} = N_{\partial, B} \beta V \left(-kT \frac{\partial}{\partial B}, B \right) w(B), \quad (3.1.11)$$

where $N_{\partial, B}$ has the same meaning as in (2.3.23).

3.1.2 Relation Between the Kinetic Potential and the Free Energy: Asymptotic Formula

The one-time equilibrium probability density $w(B)$ of internal parameters satisfies equation (2.3.41) or, otherwise, equation

$$N_{\partial, B} V \left(-kT \frac{\partial}{\partial B}, B \right) w_{\text{eq}}(B) = 0. \quad (3.1.12)$$

Let us use the formula (2.2.61) by which the probability density $w_{\text{eq}}(B)$ is expressed in terms of free energy. Substituting (2.2.61) into (3.1.12) gives

$$N_{\partial, B} V \left(-kT \frac{\partial}{\partial B}, B \right) \exp(-\beta F(B)) = 0. \quad (3.1.13)$$

Using (3.1.13), we can derive the formula connecting two macroscopic functions: free energy and kinetic potential; this formula is macroscopic in nature, i.e. it must not contain k . Consider the derivatives

$$\begin{aligned} kT \frac{\partial}{\partial B_{\alpha}} e^{-\beta F} &= - \frac{\partial F}{\partial B_{\alpha}} e^{-\beta F}, \\ (kT)^2 \frac{\partial^2}{\partial B_{\alpha_1} \partial B_{\alpha_2}} e^{-\beta F} &= \left(\frac{\partial F}{\partial B_{\alpha_1}} \frac{\partial F}{\partial B_{\alpha_2}} - kT \frac{\partial^2 F}{\partial B_{\alpha_1} \partial B_{\alpha_2}} \right) e^{-\beta F}, \\ (kT)^3 \frac{\partial^3}{\partial B_{\alpha_1} \partial B_{\alpha_2} \partial B_{\alpha_3}} e^{-\beta F} &= \\ &\left(- \frac{\partial F}{\partial B_{\alpha_1}} \frac{\partial F}{\partial B_{\alpha_2}} \frac{\partial F}{\partial B_{\alpha_3}} + kT(3) \frac{\partial^2 F}{\partial B_{\alpha_1} \partial B_{\alpha_2}} \frac{\partial F}{\partial B_{\alpha_3}} - (kT)^2 \frac{\partial^3 F}{\partial B_{\alpha_1} \partial B_{\alpha_2} \partial B_{\alpha_3}} \right) e^{-\beta F}, \end{aligned} \quad (3.1.14)$$

and so on. From these equations we have

$$\begin{aligned} & \left(-kT \frac{\partial}{\partial B_{\alpha_1}} \right) \dots \left(-kT \frac{\partial}{\partial B_{\alpha_m}} \right) \exp[-\beta F(B)] \\ &= \frac{\partial F}{\partial B_{\alpha_1}} \dots \frac{\partial F}{\partial B_{\alpha_m}} \exp[-\beta F(B)] + O(k). \end{aligned} \quad (3.1.15)$$

Using (3.1.15) and also the formulas [following from (3.1.15)]

$$\begin{aligned} & \left(-kT \frac{\partial}{\partial B_{\alpha_1}} \right) \dots \left(-kT \frac{\partial}{\partial B_{\alpha_m}} \right) K_{\alpha_1 \dots \alpha_m} \exp[-\beta F(B)] \\ &= K_{\alpha_1 \dots \alpha_m} \left(-kT \frac{\partial}{\partial B_{\alpha_1}} \right) \dots \left(-kT \frac{\partial}{\partial B_{\alpha_m}} \right) \exp[-\beta F(B)] [1 + O(k)], \end{aligned} \quad (3.1.16)$$

and omitting the terms of order k and of higher orders, from (3.1.13) we find

$$V(\partial F(B)/\partial B, B) = 0. \quad (3.1.17)$$

This is the desired formula, which is macroscopic in nature and follows from the principle of dynamic equilibrium. Formula (3.1.17) is approximate or asymptotic. The validity of both (3.1.17) and (2.2.97) is ensured by the relative smallness of the Boltzmann constant. Systems for which one can apply the asymptotic formulas must be large or macroscopic, i.e. they must contain large number of molecules, atoms, etc.

3.1.3 Example: Kinetic Potential for a System with Linear Relaxation and Quadratic Free Energy

Suppose that the system under study is described by linear macroscopic relaxation equations, which have the form

$$\dot{A}_\alpha = - \sum_\beta d_{\alpha\beta} A_\beta, \quad \alpha = 1, \dots, r. \quad (3.1.18)$$

In order that the point $A = 0$ be stable, it is necessary that the matrix $d_{\alpha\beta}$ has no eigenvalues with negative real parts. The free energy $F(A)$ must have its minimum at the stable point. We suppose that $F(A)$ is quadratic in A :

$$F(A) = \frac{1}{2} \sum_{\alpha, \beta} u_{\alpha\beta} A_\alpha A_\beta + \text{const}. \quad (3.1.19)$$

(Recall that summation over repeated subscripts is understood.) Furthermore, it is natural to suppose that the coefficients $K_{\alpha_1 \dots \alpha_m}$ are equal to zero for $m \geq 3$, so that the master equation (2.3.24) is the Fokker–Planck equation (2.3.27):

$$\frac{\partial w(B, t)}{\partial t} = - \frac{\partial}{\partial B_\alpha} [K_\alpha(B)w] + \frac{1}{2} \frac{\partial^2}{\partial B_\alpha \partial B_\beta} [K_{\alpha\beta}(B)w]. \quad (3.1.20)$$

In this case, according to (3.1.9), the kinetic potential is of the form

$$V(y, B) = K_\alpha(B)y_\alpha + (\beta/2)K_{\alpha\gamma}(B)y_\alpha y_\gamma. \quad (3.1.21)$$

Equations (3.1.18) imply that the random internal parameters vary in time in accordance with the Langevin equations

$$\dot{B}_\alpha = -d_{\alpha\beta}B_\beta + \xi_\alpha(t), \quad (3.1.22)$$

where $\xi_\alpha(t)$ are random forces with zero mean. Equations (3.1.18) can be obtained by averaging (3.1.22). Considering (3.1.22), we readily find the coefficients $K_\alpha(B)$

$$K_\alpha(B) \equiv \lim_{\tau \rightarrow 0} \frac{\langle \Delta B_\alpha \rangle_B}{\tau} = -d_{\alpha\beta}B_\beta. \quad (3.1.23)$$

Substituting (3.1.23) into (3.1.21) gives

$$V(y, B) = -d_{\alpha\gamma}y_\alpha B_\gamma + \frac{1}{2}\beta K_{\alpha\gamma}(B)y_\alpha y_\gamma. \quad (3.1.24)$$

Here the coefficients $K_{\alpha\beta}(B)$ are not yet determined. To find them let us write (3.1.17) for the case under study. Using equation $\partial F/\partial B_\alpha = u_{\alpha\delta}B_\delta$ and substituting it into (3.1.24) in place of y , we get

$$-d_{\alpha\gamma}u_{\alpha\delta}B_\delta B_\gamma + \frac{1}{2}\beta K_{\alpha\gamma}u_{\alpha\delta}u_{\gamma\epsilon}B_\delta B_\epsilon = 0. \quad (3.1.25)$$

We write $u_{\alpha\delta}B_\delta = z_\alpha$, so that $B_\delta = u_{\delta\alpha}^{-1}z_\alpha$. Hence, (3.1.25) takes the form

$$-d_{\alpha\gamma}z_\alpha u_{\gamma\rho}^{-1}z_\rho + \frac{1}{2}\beta K_{\alpha\gamma}z_\alpha z_\gamma = 0. \quad (3.1.26)$$

Differentiating (3.1.26) with respect to z_ρ and z_σ gives

$$\beta K_{\alpha\rho} = d_{\alpha\gamma}u_{\gamma\rho}^{-1} + d_{\rho\gamma}u_{\gamma\alpha}^{-1}. \quad (3.1.27)$$

Substituting (3.1.27) into (3.1.24), we finally arrive at

$$V(y, B) = d_{\alpha\gamma}y_\alpha(u_{\gamma\rho}^{-1}y_\rho - B_\gamma). \quad (3.1.28)$$

We see that the kinetic potential and, consequently, the statistics of the stationary Markov process under study is determined by two matrices $d_{\alpha\gamma}$ and $u_{\alpha\gamma}$.

3.1.4 Kinetic Potential Image

Let us introduce the ancillary probability density

$$w_x(B) = \exp(\beta x B) w_{eq}(B) / \int \exp(\beta x B') w_{eq}(B') dB'. \quad (3.1.29)$$

This probability density is the equilibrium density for the hypothetical Hamiltonian $\mathcal{H}_x(z) = \mathcal{H}(z) - xB(z)$, but not for the actual Hamiltonian $\mathcal{H}(z)$. For $\mathcal{H}_x(z)$ the free energy is

$$F_x(B) = F(B) - xB \quad (3.1.30)$$

[this equation is similar to (2.2.84)]. Applying (2.2.61) to the free energy $F_x(B)$, we have the hypothetical equilibrium probability density

$$w_x(B) = \text{const} \cdot \exp(-\beta F_x(B)) = \text{const} \cdot \exp[-\beta F(B) + \beta xB], \quad (3.1.31)$$

which coincides with (3.1.29). Since the thermodynamic forces x_α do not actually exist, the probability density (3.1.29) is a nonequilibrium one.

The image $R(y, x)$ of the kinetic potential $V(y, B)$ is defined by

$$R(y, x) = \int V(y, B) w_x(B) dB . \quad (3.1.32)$$

We note that the argument y of $R(y, x)$ has the same physical dimensions as x . In fact, from (3.1.9) (if we substitute (3.1.6) into it) it is seen that the product $\beta y_\alpha B_\alpha$ must be a dimensionless quantity. The product $\beta x_\alpha B_\alpha$ is also dimensionless. Consequently, the variable y is of the same type as x . The main distinction between $R(y, x)$ and $V(y, B)$ lies in the dimensional properties of their arguments.

Let us derive a precise formula which is a consequence of (3.1.12) for the image (3.1.32). We multiply (3.1.12) by $\exp(\beta x B)$. The last expression commutes with the operator B (i.e. with the operator of multiplication by B), but it does not commute with the operator $\partial/\partial B_\alpha$. This noncommutativity is taken into account by the formula

$$\exp(\beta x B) f(\partial/\partial B + \beta x) = f(\partial/\partial B) \exp(\beta x B) \quad (3.1.33)$$

derived in Appendix 3; see (A3.5). As a consequence of (3.1.33) we have

$$\exp(\beta x B) N_{\partial, B} V(-kT\partial/\partial B, B) = N_{\partial, B} V(-kT\partial/\partial B + x, B) \exp(\beta x B) . \quad (3.1.34)$$

We insert (3.1.34) into equation (3.1.12) or (3.1.13) multiplied by $\exp(\beta x B)$ and then we integrate both sides of the equation with respect to B over infinite space. As a result, all derivatives with respect to B vanish. This means that the term with $\partial/\partial B$ vanishes in the arguments of the kinetic potential. Then we obtain

$$\int V(x, B) \exp(\beta x B) w_{eq}(B) dB = 0 . \quad (3.1.35)$$

By virtue of (3.1.29, 32) this equation can be written as

$$R(x, x) = 0 \quad (3.1.36)$$

for all x . We will show that the equation (3.1.17) obtained earlier is the asymptotic approximation of the precise equation (3.1.36).

Since the fluctuations of B are small, the probability density $w_x(B)$ is very sharply peaked and concentrated near the point $A(x)$ of the maximum of the probability density $w_x(B)$. Therefore, from (3.1.32) we can obtain the approximate equation

$$R(y, x) = V(y, A(x)) + O(k) . \quad (3.1.37)$$

Here $A(x)$ has the inverse of the dependence of the type (2.2.97), i.e. in our case the dependence

$$\partial F(A)/\partial A_\alpha = x_\alpha . \quad (3.1.38)$$

As a consequence of (3.1.37, 38), equation (3.1.36) gives

$$V(x, A(x)) = 0 \quad (3.1.39)$$

or

$$V(\partial F(A)/\partial A, A) = 0 \quad (3.1.40)$$

for all A . The last equation is none other than (3.1.17).

We will now give some useful definitions. Substituting (3.1.9) into (3.1.32), we obtain the expansion

$$R(y, x) = \sum_{m=1}^{\infty} \frac{1}{m!} \beta^{m-1} \kappa_{\alpha_1 \dots \alpha_m}(x) y_{\alpha_1} \dots y_{\alpha_m}, \quad (3.1.41)$$

where we have denoted

$$\kappa_{\alpha_1 \dots \alpha_m}(x) = \int K_{\alpha_1 \dots \alpha_m}(B) w_x(B) dB. \quad (3.1.42)$$

The functions (3.1.42) can be called the images of the coefficient functions.

In conclusion of this subsection we will give several formulas related to (3.1.38). Substituting equation (2.2.84), i.e. the equation

$$F(A) = F_0(A) - A a^0 \quad (3.1.43)$$

(here the equilibrium values of external parameters are denoted by a_α^0), into (3.1.38), we obtain

$$x_\alpha + a_\alpha^0 = \partial F_0(A)/\partial A_\alpha. \quad (3.1.44)$$

Setting $x = 0$, we have

$$a_\alpha^0 = \partial F_0(A^0)/\partial A_\alpha^0, \quad (3.1.45)$$

where the equilibrium mean values of internal parameters are denoted by A_α^0 . If we pass to nonzero values of x , it is convenient to treat $a_\alpha^0 + x_\alpha$ as the nonequilibrium values a_α :

$$x_\alpha + a_\alpha^0 = a_\alpha. \quad (3.1.46)$$

Then (3.1.44) can be written in the form

$$a_\alpha = \partial F_0(A)/\partial A_\alpha, \quad (3.1.47)$$

which is analogous to (3.1.45). We note that (2.2.96) is valid for both equilibrium and nonequilibrium values of the parameters, i.e. both the following equations are valid:

$$\begin{aligned} dF_0(A^0) &= -S dT + a_\alpha^0(T, A^0) dA_\alpha^0, \\ dF_0(A) &= -S dT + a_\alpha(T, A) dA_\alpha. \end{aligned} \quad (3.1.48)$$

In certain cases $a_\alpha^0 = 0$; then the thermodynamic forces x_α coincide with the external parameters a_α according to (3.1.46).

3.1.5 Modified Kinetic Potential

The definition of kinetic potential by means of (3.1.9) or (3.1.10) is useful only in the free energy version of the theory when formula (2.2.61) is taken as the basic one. In

the entropy version the one-time equilibrium probability density is determined by entropy [see (2.2.65) or (2.2.107)]. In this case it is expedient to modify the definition of the kinetic potential and, instead of (3.1.10), to define it by

$$\Phi(v, B) = k^{-1} V'(kv, B). \quad (3.1.49)$$

In the same way as before one can verify that instead of (3.1.17) [in the case of (2.2.65)] we have

$$V'(-\partial S(B)/\partial B, B) = 0. \quad (3.1.50)$$

In this case the image $R'(X, B)$ is defined by the formula

$$R'(Y, X) = \int V'(Y, B) w_X(B) dB, \quad (3.1.51)$$

which is analogous to (3.1.32). Here

$$w_X(B) = \text{const} \cdot \exp(XB/k) w_{eq}(B) = \text{const} \cdot \exp[(S(B) + XB)/k]. \quad (3.1.52)$$

Multiplying (3.1.12) by $\exp(XB/k)$, transposing the last expression from the left-hand side to the right-hand side and integrating the result with respect to B (using essentially the same method as before), we can obtain

$$R'(X, X) = 0. \quad (3.1.53)$$

This exact equation is nothing but a modified version of (3.1.36).

In the last version the analogues of (3.1.41, 42) have the form

$$R'(Y, X) = \sum_{m=1}^{\infty} \frac{1}{m!} k^{-m+1} \lambda_{\alpha_1 \dots \alpha_m}(X) Y_{\alpha_1} \dots Y_{\alpha_m}, \quad (3.1.54)$$

where

$$\lambda_{\alpha_1 \dots \alpha_m}(X) = \int K_{\alpha_1 \dots \alpha_m}(B) w_X(B) dB. \quad (3.1.55)$$

In conclusion we write the asymptotic equation

$$R'(Y, X) = V'(Y, \bar{A}(X)) + \mathcal{O}(k), \quad (3.1.56)$$

which is analogous to (3.1.37). This follows from (3.1.51) in the case of the sharp probability density $w_X(B)$. Here

$$\bar{A}_{\alpha}(X) = \int B_{\alpha} w_X(B) dB. \quad (3.1.57)$$

However, instead of (3.1.57), one can equally well take the values A_{α}^0 at which the probability density (3.1.52) has its maximum since the difference between A_{α}^0 and \bar{A}_{α} is small: $A_{\alpha}^0 - \bar{A}_{\alpha} \sim k$. The point where $w_X(B)$ has the maximum is determined by the equation $\partial w_X(B)/\partial B = 0$, i.e.

$$X_{\alpha} = -\partial S(A)/\partial A_{\alpha}. \quad (3.1.58)$$

If in (3.1.56) the dependence $A^0(X)$, which is the inverse of the dependence (3.1.58),

is taken instead of $\bar{A}(X)$, then after changing variables we have

$$\bar{V}(Y, A) = \bar{R} \left[Y, -\frac{\partial S(A)}{\partial A} \right] + \mathcal{O}(k). \quad (3.1.59)$$

In the same way, from (3.1.55) we get, approximately,

$$K_{\alpha_1 \dots \alpha_m}(A) = A_{\alpha_1 \dots \alpha_m} \left(-\frac{\partial S(A)}{\partial A} \right). \quad (3.1.60)$$

Of course, from (3.1.51, 55) one can obtain more accurate asymptotic equations than (3.1.59, 60).

When (2.2.107) is valid instead of (2.2.65), we have

$$w_X(B) = \text{const} \cdot \exp \{k^{-1}[S(B) + B\alpha^0 + BX]\}. \quad (3.1.61)$$

Here we have denoted the equilibrium values of the parameter α appearing in (2.2.107) by the superscript “0”. From (3.1.61) we see that the addition of the term BX results in the fact that the equilibrium values α_i^0 are replaced by the non-equilibrium values

$$\alpha_i = \alpha_i^0 + X_i, \quad i = 0, 1, \dots, r. \quad (3.1.62)$$

From the condition $\partial w_X(B)/\partial B_i = 0$, and by virtue of (3.1.61), we obtain

$$-\frac{\partial S(B)}{\partial B_i} = \alpha_i^0 + X_i, \quad (3.1.63)$$

i.e. for the nonequilibrium case the derivatives $-\partial S(B)/\partial B_i$ coincide with the nonequilibrium values given by (3.1.62). Equation (3.1.62) is the k -version of (3.1.46).

For the probability density (3.1.61) the dependence $\bar{A}(X) \approx A^0(X)$ in (3.1.56) is the inverse of the dependence (3.1.63) at $B = \bar{A}$. But by virtue of (2.2.108) and owing to the negligible difference between $\bar{S}(A)$ and $S(B)$, the dependence $A = -\partial \Gamma(\alpha)/\partial \alpha$ is the inverse of the dependence $\alpha = -\partial S(B)/\partial B$. Therefore,

$$\bar{A}_i(X) = -\frac{\partial \Gamma}{\partial \alpha_i}(\alpha^0 + X), \quad (3.1.64)$$

and (3.1.56) takes the form

$$\bar{R}(Y, X) = \bar{V} \left(Y, -\frac{\partial \Gamma}{\partial \alpha}(\alpha^0 + X) \right). \quad (3.1.65)$$

Consequently, in the case described by (3.1.61) equation (3.1.53) can be written as

$$\bar{V} \left(X, -\frac{\partial \Gamma}{\partial \alpha}(\alpha^0 + X) \right) = 0. \quad (3.1.66)$$

3.1.6 Properties of the Kinetic Potential and of Its Image

Both the kinetic potential (3.1.9) and the modified kinetic potential (3.1.49) have similar properties, which we now consider. Let us study the potential (3.1.9) as an example.

Substituting (3.1.2) into (3.1.9) gives

$$V(y, B) = \lim_{\tau \rightarrow 0} \left\{ \tau^{-1} \sum_{m=1}^{\infty} \frac{1}{m!} \beta^{m-1} \langle (y_\alpha \Delta B_\alpha)^m \rangle_B \right\}. \quad (3.1.67)$$

Obviously, this equation can be written in the form

$$V(y, B) = kT \lim_{\tau \rightarrow 0} [\tau^{-1} \langle \exp(\beta y \Delta B) - 1 \rangle_B]. \quad (3.1.68)$$

Differentiating (3.1.68) with respect to y_α and y_γ , we find the matrix of the second derivatives

$$\frac{\partial^2 V(y, B)}{\partial y_\alpha \partial y_\gamma} = \beta \lim_{\tau \rightarrow 0} \{ \tau^{-1} \langle \Delta B_\alpha \Delta B_\gamma \exp(\beta y \Delta B) \rangle_B \}. \quad (3.1.69)$$

Using (3.1.69), we easily prove that for any y_α this matrix is nonnegative definite and, consequently, the potential $V(y, B)$ is a convex function of the variables y . As is well known, the condition of nonnegative definiteness of the matrix $V_{\alpha\gamma}$ has the form

$$V_{\alpha\gamma} a_\alpha a_\gamma \geq 0. \quad (3.1.70)$$

This inequality must be satisfied for any a_1, a_2, \dots . For the matrix (3.1.69) the expression $V_{\alpha\gamma} a_\alpha a_\gamma$ takes the form

$$\frac{\partial^2 V(y, B)}{\partial y_\alpha \partial y_\gamma} a_\alpha a_\gamma = \beta \lim_{\tau \rightarrow 0} \{ \tau^{-1} \langle (a_\alpha \Delta B_\alpha)^2 \exp(\beta y \Delta B) \rangle_B \}. \quad (3.1.71)$$

The expression inside the sign $\langle \dots \rangle$ in (3.1.71) is nonnegative for any a and τ . Therefore, (3.1.71) is always nonnegative. This proves that the matrix (3.1.69) is nonnegative definite and the kinetic potential is convex with respect to y .

From the convexity just proved it follows that the cut-off potential

$$\begin{aligned} V_f(y, B) &= V(y, B) - K_\alpha(B) y_\alpha \\ &= \sum_{m=2}^{\infty} \frac{1}{m!} \beta^{m-1} K_{\alpha_1 \dots \alpha_m}(B) y_{\alpha_1} \dots y_{\alpha_m}, \end{aligned} \quad (3.1.72)$$

which is determined only by the diffusion coefficients $K_{\alpha\beta}(B)$, $K_{\alpha\beta\gamma}(B)$, ... and which is consequently caused by fluctuations, has the property $V_f(y, B) \geq 0$. In fact, according to (3.1.72), we have

$$V_f(0, B) = 0, \quad \partial V_f(y, B) / \partial y_\alpha = 0 \quad \text{for } y = 0. \quad (3.1.73)$$

Consequently, in the $(r+1)$ -dimensional space with coordinates y_0, y_1, \dots, y_r , the hyperplane $y_0 = 0$ is tangential to the hypersurface $y_0 = V_f(y, B)$ (here the coordinates B are fixed). Since the latter is convex, it does not cross the hyperplane and lies above it. This proves that V_f is nonnegative.

The proof can be performed directly, without using the convex property. From (3.1.72, 68) we have

$$V_f(y, B) = kT \lim_{\tau \rightarrow 0} [\tau^{-1} \langle f(y \Delta B) \rangle_B], \quad (3.1.74)$$

where

$$f(x) = \exp(\beta x) - 1 - \beta x . \quad (3.1.75)$$

The nonnegativity of the limit (3.1.74) immediately follows from the nonnegativity of the function $f(x)$.

The image (3.1.41) also has the property of convexity with respect to y at fixed x . Using (3.1.6, 42), we see that the functions $\kappa_{\alpha_1 \dots \alpha_m}(x)$ can be represented in the form

$$\kappa_{\alpha_1 \dots \alpha_m}(x) = \lim_{\tau \rightarrow 0} [\tau^{-1} \langle \Delta B_{\alpha_1} \dots \Delta B_{\alpha_m} \rangle_x] , \quad (3.1.76)$$

where

$$\langle \dots \rangle_x = \int \langle \dots \rangle_B w_x(B) dB . \quad (3.1.77)$$

Substituting (3.1.76) into (3.1.41), we obtain the formula

$$R(y, x) = kT \lim_{\tau \rightarrow 0} [\tau^{-1} \langle \exp(\beta y \Delta B) - 1 \rangle_x] , \quad (3.1.78)$$

which is analogous to (3.1.68). By using it we can prove the convexity quite analogously with the former proof. The property

$$R_f(y, x) \geq 0 \quad (3.1.79)$$

of the fluctuational part

$$R_f(y, x) = \sum_{m=2}^{\infty} \frac{1}{m!} \beta^{m-1} \kappa_{\alpha_1 \dots \alpha_m}(x) y_{\alpha_1} \dots y_{\alpha_m} \quad (3.1.80)$$

can also be proved in an analogous way.

3.2 Consequences of Time Reversibility

3.2.1 Time-Reversal Symmetry of the Hamiltonian and of the One-Time Probability Density

Equation (3.1.17) restricts the kinetic potential and, consequently, the Markov operator. The time reversibility of the stationary Markov process $B(t)$ restricts the kinetic potential much more.

We now consider the time reversibility or, in other words, the invariance under the time reversal transformation, i.e. under the replacement of t by $\tilde{t} = -t + \text{const}$. The system S under study is reversible in time if its Hamiltonian function $\mathcal{H}(z)$ is invariant under change of variables $z \rightarrow \tilde{z}$, where

$$\begin{aligned} \tilde{z} &= \varepsilon z \\ &= (\varepsilon_1 q_1, \varepsilon_2 q_2, \dots, \varepsilon_{n+1} p_1, \varepsilon_{n+2} p_2, \dots) \\ &= (q_1, q_2, \dots, -p_1, -p_2, \dots) . \end{aligned}$$

Here $\varepsilon_i = 1$ for generalized coordinates q_i since the coordinates are supposed to be time-even, i.e. they do not change sign under time reversal transformation. In contrast, momenta change sign and for them $\varepsilon_i = -1$, $i > n$.

The condition of time reversibility of the system S can thus be written

$$\mathcal{H}(\varepsilon z) = \mathcal{H}(z). \quad (3.2.1)$$

This condition means that the Hamiltonian function is even in momenta and independent of time-odd parameters. Condition (3.2.1) is fulfilled for a great many cases, but not always. For example, it is not valid when the system under study is located in an external magnetic field \mathbf{H} which changes sign under the time-reversal transformation. The Hamiltonian function depends on this field as a parameter. Therefore, the equation $\mathcal{H}(\varepsilon z, -\mathbf{H}) = \mathcal{H}(z, \mathbf{H})$, and not (3.2.1), must hold in the given case. Similar cases will be discussed later (Sect. 4.1.4). It is obvious that the time reversal transformation is purely imaginary since one cannot manipulate time in reality.

From condition (3.2.1) we easily derive the result that Hamilton's equations

$$\frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i} \quad (3.2.2)$$

describing the change of the system with time remain invariant under the time-reversal transformation, i.e. in reversed time the same equations are valid:

$$\frac{d\tilde{q}_i}{d\tilde{t}} = \frac{\partial \mathcal{H}}{\partial \tilde{p}_i}, \quad \frac{d\tilde{p}_i}{d\tilde{t}} = -\frac{\partial \mathcal{H}}{\partial \tilde{q}_i}. \quad (3.2.3)$$

We now suppose that the internal thermodynamic parameters $B = (B_1, \dots, B_r)$ are the eigenfunctions of the time-reversal operator, i.e. they satisfy the equations

$$B_\alpha(\varepsilon z) = \varepsilon_\alpha B_\alpha(z), \quad \alpha = 1, \dots, r, \quad (3.2.4)$$

where ε_α are certain numbers. Since the repeated application of the same operator leads to the initial functions, the numbers ε_α must satisfy the condition $\varepsilon_\alpha^2 = 1$, i.e. they must be equal to +1 or to -1. If $\varepsilon_\alpha = 1$, the corresponding parameter B_α is called time-even and, if $\varepsilon_\alpha = -1$, the parameter B_α is called time-odd. The assumption of the validity of (3.2.4) does not essentially limit the generality since, if (3.2.4) is invalid, one should switch over to parameters

$$B_\alpha(z) \pm B_\alpha(\varepsilon z),$$

which satisfy an equation of the type (3.2.4).

We now consider the one-time equilibrium probability density of internal parameters:

$$w(B) = \int \delta(B(z) - B) w(z) dz. \quad (3.2.5)$$

Here $w(z)$ is the probability density (2.2.5) or (2.2.6). In all cases, (3.2.1) ensures that this probability density is symmetrical in time, i.e.

$$w(\varepsilon z) = w(z). \quad (3.2.6)$$

We easily verify that the following equation is valid:

$$w(\varepsilon B) = w(B) . \quad (3.2.7)$$

In fact, using (3.2.4, 5), we have

$$\begin{aligned} w(\varepsilon B) &= \int \delta(B(z) - \varepsilon B) w(z) dz \\ &= \int \delta(B(\varepsilon z) - B) w(z) dz \end{aligned} \quad (3.2.8)$$

(the evenness of $\delta(x)$ is used). Changing the integration variable on the right-hand side, we obtain

$$w(\varepsilon B) = \int \delta(B(\tilde{z}) - B) w(\varepsilon \tilde{z}) d\tilde{z} , \quad (3.2.9)$$

which coincides with (3.2.5) by virtue of (3.2.6).

3.2.2 Conditions Imposed on Transition Probabilities by Time Reversibility

We now proceed to the two-time probability density

$$w_{t_2 t_1}(B_2, B_1) = \int \delta(B(z(t_2)) - B_2) \delta(B(z(t_1)) - B_1) w(z(t_1)) dz(t_1) , \quad (3.2.10)$$

where $t_2 - t_1 = \tau > 0$, $z(t_2) = \varphi_\tau(z(t_1))$; the last function is determined by (3.2.2).

We now switch over to reverse time, which is defined by the equation $\tilde{t} = \tilde{t}(t) = -t + \text{const}$. In reverse time the moments $\tilde{t}(t_1)$ and $\tilde{t}(t_2)$ correspond to the moments of time t_1 and t_2 , $t_1 < t_2$. The larger of $\tilde{t}(t_1)$ and $\tilde{t}(t_2)$ is denoted by t_+ and the other one is denoted by t_- . The earliest moment in forward time becomes the latest in reverse time and vice versa. Hence,

$$\begin{aligned} t_+ &= \tilde{t}(t_1) = -t_1 + \text{const} , \\ t_- &= \tilde{t}(t_2) = -t_2 + \text{const} . \end{aligned} \quad (3.2.11)$$

If the constant is assumed to be equal to $t_2 + t_1$, then from (3.2.11) we obtain

$$t_+ = t_2, \quad t_- = t_1 . \quad (3.2.12)$$

Let us write the probability density analogous to (3.2.10) in reverse time. It is of the form

$$\begin{aligned} \tilde{w}_{t_+ t_-}(\tilde{B}_2, \tilde{B}_1) &= \int \delta\{\tilde{B}[\tilde{z}(t_+)] - \tilde{B}_2\} \delta\{\tilde{B}[\tilde{z}(t_-)] - \tilde{B}_1\} \\ &\quad \times w[\tilde{z}(t_-)] d\tilde{z}(t_-) . \end{aligned} \quad (3.2.13)$$

In writing (3.2.10, 13) we have assumed that $B(t) = B(z(t))$ and $\tilde{B}(\tilde{t}) = \tilde{B}(\tilde{z}(\tilde{t}))$, i.e. that the changes in the internal parameters are induced only by the changes in the dynamic parameters in both forward and reverse times. In the presence of time-reversal symmetry the changes in the dynamic variables in forward and reverse

times are described by equations (3.2.2, 3) having identical forms and the stationary probability density in forward time is the same as that in reverse time. Therefore, expression (3.2.10) must be the same function of $t_2 - t_1$, B_2, B_1 as expression (3.2.13) is of $t_+ - t_-, \tilde{B}_2, \tilde{B}_1$. Hence, denoting this function by $f_\tau(B_2, B_1)$, we have

$$\langle \delta(B(t_2) - B_2) \delta(B(t_1) - B_1) \rangle = f_\tau(B_2, B_1), \quad (3.2.14)$$

$$\langle \delta[\tilde{B}(t_+) - \tilde{B}_2] \delta[\tilde{B}(t_-) - \tilde{B}_1] \rangle = f_\tau(\tilde{B}_2, \tilde{B}_1). \quad (3.2.15)$$

We now use the relation between the functions $\tilde{B}(t)$ and $B(t)$. Considering the quantities ε_α in (3.2.4), we obtain

$$\tilde{B}_\alpha(\tilde{t}(t)) = \varepsilon_\alpha B_\alpha(t). \quad (3.2.16)$$

Setting $t = t_2$ and then $t = t_1$, and using (3.2.11), we get

$$\tilde{B}_\alpha(t_+) = \varepsilon_\alpha B_\alpha(t_1), \quad \tilde{B}_\alpha(t_-) = \varepsilon_\alpha B_\alpha(t_2). \quad (3.2.17)$$

Consequently, (3.2.15) can be written as

$$\langle \delta(\varepsilon B(t_1) - \tilde{B}_2) \delta(\varepsilon B(t_2) - \tilde{B}_1) \rangle = f_\tau(\tilde{B}_2, \tilde{B}_1) \quad (3.2.18)$$

or (using $\tilde{B}_i = \varepsilon B_i$)

$$\langle \delta(B(t_1) - B_2) \delta(B(t_2) - B_1) \rangle = f_\tau(\varepsilon B_2, \varepsilon B_1) \quad (3.2.19)$$

since $\delta(\varepsilon x) = \delta(x)$.

If we here replace B_2 by B_1 and B_1 by B_2 , the expressions on the left-hand sides of (3.2.14, 19) will be identical. Consequently,

$$f_\tau(\varepsilon B_1, \varepsilon B_2) = f_\tau(B_2, B_1). \quad (3.2.20)$$

This equation and, therefore, by virtue of (3.2.10, 14) the equation

$$w_\tau(\varepsilon B_1, \varepsilon B_2) = w_\tau(B_2, B_1), \quad (3.2.21)$$

indicates the restriction imposed on the two-time probability density by the condition of time reversibility.

From (3.2.21) we easily obtain the restriction imposed on the transition probabilities

$$w_\tau(B_2 | B_1) = w_\tau(B_2, B_1) / w(B_1). \quad (3.2.22)$$

Considering (3.2.7, 22), we find from (3.2.21) that

$$w_\tau(\varepsilon B_1 | \varepsilon B_2) w(B_2) = w_\tau(B_2 | B_1) w(B_1), \quad (3.2.23)$$

where $\tau > 0$ and $w(B)$ is the equilibrium one-time probability density. Equation (3.2.21) or (3.2.23) can be regarded as the definition of detailed balance.

3.2.3 Time-Reversal and the Markov Operator

Let us now consider the Markov operator

$$L = N_{\partial, B} \beta V \left(-kT \frac{\partial}{\partial B}, B \right) \quad (3.2.24)$$

appearing in (3.1.11). If we introduce the matrix elements $L_{BB'}$ of the operator L , its operation can be written in the form of an integral:

$$Lf(B) = \int L_{BB'} f(B') dB' \quad (3.2.25)$$

($f(B)$ is an arbitrary function).

According to the derivation of the master equation in Sect. 2.3.3, the matrix $L_{BB'}$ is defined by

$$L_{BB'} = \lim_{\tau \rightarrow 0} \{ \tau^{-1} [w_\tau(B|B') - \delta(B - B')] \}. \quad (3.2.26)$$

In fact, if we proceed not from (2.3.17), but from the equivalent equation (2.3.10), formula (2.3.19) will be of the form

$$\begin{aligned} & \tau^{-1} [w_{t_3 t_1}(B|B'') - w_{t_2 t_1}(B|B'')] \\ &= \tau^{-1} \left\{ \int [w_{t_3 t_2}(B|B') - \delta(B - B')] w_{t_2 t_1}(B'|B'') dB' \right\} \end{aligned} \quad (3.2.27)$$

(we have replaced y by B). Hence, by passing to the limit $\tau \rightarrow 0$, we obtain the master equation

$$\frac{d}{dt} w_{tt_1}(B|B'') = \int L_{BB'} w_{tt_1}(B'|B'') dB' \equiv L w_{tt_1}(B|B''), \quad (3.2.28)$$

where $L_{BB'}$ is defined by (3.2.26).

Let us find the restrictions imposed on the Markov operator by the condition of time reversibility (or of detailed balance). Equation (3.2.23) is equivalent to

$$\tau^{-1} [w_\tau(\varepsilon B_1 | \varepsilon B_2) - \delta(B_1 - B_2)] w(B_2) = \tau^{-1} [w_\tau(B_2 | B_1) - \delta(B_2 - B_1)] w(B_1) \quad (3.2.29)$$

since $\delta(B_1 - B_2) w(B_2) = \delta(B_1 - B_2) w(B_1)$. Taking the limit $\tau \rightarrow 0$ in (3.2.29) and considering (3.2.26), we obtain

$$[1/w(B')] L_{\varepsilon B', \varepsilon B} w(B) = L_{BB'}, \quad (3.2.30)$$

where $B = B_2$ and $B' = B_1$. On the left-hand side of the last equation we have the Markov operator in reverse time, and on its right-hand side we have the Markov operator in forward time; they must coincide due to time symmetry. We see that the Markov operator in reverse time can be obtained from the Markov operator in forward time by three operations: (1) by substitution of B and B' by εB and $\varepsilon B'$, (2) by transposition of the matrix $L_{BB'}$, and (3) by multiplication of L^T by $w(B)$ from the right and by $w^{-1}(B)$ from the left. This rule was originally given by *Kolmogorov* [3.1]. Using the notation $(L_{BB'})_\varepsilon = L_{\varepsilon B, \varepsilon B'}$, we can write (3.2.30) in a shorter form:

$$w(B)(L)_\varepsilon^T = L w(B). \quad (3.2.31)$$

Here $w(B)$ plays the role of the operator of multiplication by this function.

3.2.4 Restrictions Imposed on the Kinetic Potential and on Its Image

As a consequence of (3.2.24) the matrix elements $L_{BB'}$ can be written as

$$L_{BB'} = \beta V\left(-kT \frac{\partial}{\partial B}, B'\right) \delta(B - B'). \quad (3.2.32)$$

This can be verified with the help of (3.2.25).

Using (3.2.32), we easily find the matrix elements $L_{\varepsilon B, \varepsilon B'}$ of the operator $\{L\}_\varepsilon$:

$$L_{\varepsilon B, \varepsilon B'} = \beta V\left(-kT \frac{\partial}{\varepsilon \partial B}, \varepsilon B'\right) \delta(\varepsilon B - \varepsilon B'). \quad (3.2.33)$$

Since $\delta(\varepsilon B - \varepsilon B') = \delta(B - B')$ due to evenness of the δ -function, we obtain from (3.2.33)

$$\{L\}_\varepsilon = N_{\partial, B} \beta V\left(-kT, \frac{\partial}{\varepsilon \partial B}, \varepsilon B\right).$$

Let us transpose the last operator. When we carry out the transposition, the operator ordering is reversed. Besides $(\partial/\partial B_\alpha)^T = -\partial/\partial B_\alpha$. Therefore, we have

$$\{L\}_\varepsilon^T = N_{B, \partial} \beta V\left(kT \frac{\partial}{\varepsilon \partial B}, \varepsilon B\right). \quad (3.2.34)$$

Here $N_{B, \partial}$ indicates the operator ordering that is the inverse of the ordering $N_{\partial, B}$. By virtue of (3.2.24, 34), formula (3.2.31) gives

$$N_{B, \partial} \left[V\left(kT \frac{\partial}{\varepsilon \partial B}, \varepsilon B\right) w(B) \right] = N_{\partial, B} V\left(-kT \frac{\partial}{\partial B}, B\right) w(B), \quad (3.2.35)$$

where B is regarded as the operator of multiplication by B . We now use the operator formula

$$N_{\partial, B} f(\partial/\partial B, B) = N_{B, \partial} \tilde{f}(\partial/\partial B, B), \quad (3.2.36)$$

where

$$\bar{f}(x, y) = \exp\left(\frac{\partial^2}{\partial x \partial y}\right) f(x, y) \quad (3.2.37)$$

$(\partial^2/\partial x \partial y = \Sigma \partial^2/\partial x_\alpha \partial y_\alpha; x$ and y are C -numbers). This formula is proved in Appendix 3 [see (A3.9, 14)].

Letting $f(u, B) = V(-kTu, B)w(B)$ and using (3.2.36), we transform (3.2.35) to the form

$$N_{B, \partial} V\left(kT \frac{\partial}{\varepsilon \partial B}, \varepsilon B\right) w(B) = N_{B, \partial} \tilde{f}\left(\frac{\partial}{\partial B}, B\right), \quad (3.2.38)$$

where

$$\tilde{f}(u, B) = \exp\left(\frac{\partial^2}{\partial u \partial B}\right) [V(-kTu, B)w(B)]. \quad (3.2.39)$$

Since we now have the same operator ordering in both parts of (3.2.38), the functions must coincide:

$$V(kT\epsilon u, \epsilon B)w(B) = \tilde{f}(u, B) . \quad (3.2.40)$$

From (3.2.39, 40) we have

$$\exp\left(\frac{\partial^2}{\partial u \partial B}\right)[V(-kTu, B)w(B)] = V(kT\epsilon u, \epsilon B)w(B) \quad (3.2.41)$$

or

$$\exp\left(-kT \frac{\partial^2}{\partial y \partial B}\right)[V(y, B)w(B)] = V(-\epsilon y, \epsilon B)w(B) \quad (3.2.42)$$

if we write $-kTu = y$. The last formula imposes the restriction (caused by time symmetry) on the kinetic potential $V(y, B)$. The formula for the image $R(y, x)$ corresponding to (3.2.42) is simpler. Let us multiply (3.2.42) by $\text{const} \cdot \exp(\beta xB)$. According to (3.1.33), we have

$$\exp(\beta xB) \exp\left(-kT \frac{\partial^2}{\partial y \partial B}\right) = \exp\left[-kT \frac{\partial}{\partial y} \left(\frac{\partial}{\partial B} - \beta x\right)\right] \exp(\beta xB) . \quad (3.2.43)$$

Therefore, formula (3.2.42) multiplied by $\text{const} \cdot \exp(\beta xB)$ can be written as

$$\exp\left(-kT \frac{\partial^2}{\partial y \partial B} + x \frac{\partial}{\partial y}\right)[V(y, B)w_x(B)] = V(-\epsilon y, \epsilon B)w_x(B) \quad (3.2.44)$$

[$w_x(B)$ has been defined by (3.1.29)].

If both sides of this equation are integrated with respect to B , then all derivatives $\partial/\partial B$ will drop out and we shall have

$$\int \exp\left(x \frac{\partial}{\partial y}\right)[V(y, B)w_x(B)] dB = \int V(-\epsilon y, \epsilon B)w_x(B) dB . \quad (3.2.45)$$

Using the definition (3.1.32) of the kinetic potential image, we can write

$$\exp\left(x \frac{\partial}{\partial y}\right)R(y, x) = R(-\epsilon y, \epsilon x) . \quad (3.2.46)$$

In fact, we have

$$\begin{aligned} \int V(-\epsilon y, \epsilon B)w_x(B) dB &= \int V(-\epsilon y, \tilde{B})w_x(\epsilon \tilde{B}) d\tilde{B} \\ &= \int V(-\epsilon y, \tilde{B})w_{xx}(\tilde{B}) d\tilde{B} \\ &= R(-\epsilon y, \epsilon x) \end{aligned} \quad (3.2.47)$$

since $w_{xx}(\epsilon B) = w_x(B)$ on account of (3.2.7) and (3.1.29). If the formula

$$\exp\left(x \frac{\partial}{\partial y}\right)\varphi(y) = \varphi(y + x) , \quad (3.2.48)$$

which is none other than the Taylor expansion

$$\varphi(y + x) = \varphi(y) + \sum_{n=1}^{\infty} \frac{x^n}{n!} \frac{\partial^n \varphi(y)}{\partial y^n}, \quad (3.2.49)$$

is used, then (3.2.46) transforms to the form

$$R(y + x, x) = R(-\varepsilon y, \varepsilon x) \quad (3.2.50)$$

for arbitrary x, y . This equation resulting from time-reversal symmetry is the basic generating equation of Markov nonlinear nonequilibrium thermodynamics. We see that it is simpler than the equivalent generating equation (3.2.42). To obtain this simplification, the image of kinetic potential has been introduced.

Note that besides the precise equation (3.2.35) the approximate equation can be written as

$$V\left(y + \frac{\partial F(B)}{\partial B}, B\right) = V(-\varepsilon y, \varepsilon B). \quad (3.2.51)$$

Its validity, like that of (3.1.17), is dependent upon the smallness of k .

3.2.5 The Modified Generating Equation

Calculations analogous to the previous ones can be carried out for the modified kinetic potential defined in Sect. 3.1.5. Instead of (3.2.35) we can obtain

$$N_{B,\partial} \left[V'\left(k \frac{\partial}{\partial B}, \varepsilon B\right) \right] w(B) = N_{\partial,B} V'\left(-k \frac{\partial}{\partial B}, B\right) w(B). \quad (3.2.52)$$

The formula

$$\exp\left(-k \frac{\partial^2}{\partial Y \partial B}\right) [V'(Y, B) w(B)] = V'(-\varepsilon Y, \varepsilon B) w(B) \quad (3.2.53)$$

is the analogue of (3.2.42). Multiplying (3.2.53) by $\text{const} \cdot \exp(XB/k)$, integrating it with respect to B and considering (3.1.51, 52), we get

$$R'(Y + X, X) = R'(-\varepsilon Y, \varepsilon X) \quad (3.2.54)$$

in complete analogy with the previous calculations. Equation (3.2.54) is the modification of the generating equation (3.2.50).

In conclusion we note that (3.1.53) results from (3.2.54) [as (3.1.36) results from (3.2.50)]. In fact, setting $Y = 0$ in (3.2.54), we get

$$R'(X, X) = R'(0, \varepsilon X). \quad (3.2.55)$$

But $R'(0, \varepsilon X) = 0$ as one can see from (3.1.54). Consequently, (3.2.55) gives (3.1.53).

Thus, the generating equations (3.2.50, 54) are more restrictive than equations (3.1.36, 53), which are the consequences only of the stationary equation (2.3.41).

3.3 Examples of the Kinetic Potential and of the Validity of the Generating Equation

3.3.1 Consequences of the Generating Equation for a System with Linear Relaxation and Quadratic Free Energy

For the system described by the linear phenomenological relaxation equations (3.1.18) the kinetic potential is of the form (3.1.28). Substituting this expression into (3.1.32), we find the image corresponding to the given case:

$$R(y, x) = d_{\alpha\gamma} y_\alpha (u_{\gamma\rho}^{-1} y_\rho - A_\gamma(x)). \quad (3.3.1)$$

The dependence $A(x)$ is the inverse of the dependence $x(A)$ obtained by substituting the free energy (3.1.19) into (3.1.38). After this substitution we have

$$x_\alpha(A) = u_{\alpha\beta} A_\beta, \quad \text{i.e.} \quad A_\beta(x) = u_{\beta\alpha}^{-1} x_\alpha. \quad (3.3.2)$$

Hence, the function (3.3.1) takes the form

$$R(y, x) = d_{\alpha\gamma} u_{\gamma\rho}^{-1} y_\alpha (y_\rho - x_\rho). \quad (3.3.3)$$

Substituting (3.3.3) into (3.2.50) gives

$$d_{\alpha\gamma} u_{\gamma\rho}^{-1} (y_\alpha + x_\alpha) y_\rho = \varepsilon_\alpha d_{\alpha\gamma} u_{\gamma\rho}^{-1} \varepsilon_\rho y_\alpha (y_\rho + x_\rho). \quad (3.3.4)$$

This equation holds for any y and x . Consequently, we have

$$d_{\rho\gamma} u_{\gamma\alpha}^{-1} = \varepsilon_\alpha \varepsilon_\rho d_{\alpha\gamma} u_{\gamma\rho}^{-1}. \quad (3.3.5)$$

Equations (3.3.5) are equivalent to the Onsager–Casimir relations (4.1.11), which will be considered later.

3.3.2 Diode Model of a Nonlinear Resistor: Relaxation Equation

Consider an electric circuit consisting of a nonlinear resistor and capacitor (Fig. 3.1). The capacitance C can be the stray capacitance of the nonlinear resistor or the sum of the capacitor capacitance and the stray capacitance. The nonlinear resistor is assumed to be constructed as an ideal vacuum diode (Fig. 3.2). We

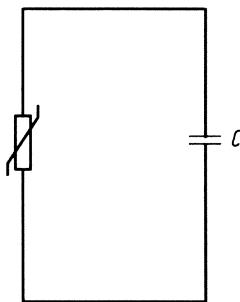


Fig. 3.1. Simple electric circuit with a nonlinear resistor

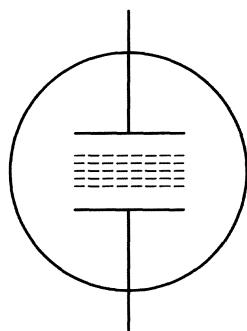


Fig. 3.2. Diode with space charge; this serves as a model of a nonlinear resistor

suppose that there is a stationary (fixed) negative space charge in the space between the electrodes. It creates an electric field described by electric potential $\varphi(x)$, where x is the coordinate normal to the surface of plane-parallel electrodes. In Fig. 3.3a the qualitative behaviour of the function $-e\varphi(x)$ ($e > 0$) is shown in the case of zero potential difference across the electrodes. The points A and B denote the position of electrode surfaces. The jump of the function $-e\varphi(x)$ nearby electrode surfaces corresponds to the work function of the electrode metal. If there is a potential difference across the electrodes, the function $-e\varphi(x)$ has the form shown in Fig. 3.3b.

We denote the charge on the capacitor by Q and the potential difference across the electrodes by $V = Q/C$. The distance between the electrodes is denoted by d . A force

$$f(x) = -eE(x) = e \frac{d\varphi(x)}{dx} + \frac{eV}{d} = e \frac{d\varphi(x)}{dx} + \frac{eQ}{Cd} \quad (3.3.6)$$

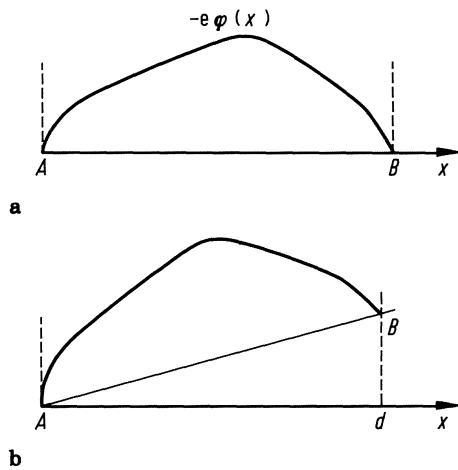


Fig. 3.3a, b. Behaviour of the potential inside the diode (a) without an external voltage and (b) with an external voltage

acts on electrons at point x ($0 < x < d$). We now take into account that the charge Q on the electrodes changes due to the electron motion. Let an electron move from the left to the right. When the electron is at the left electrode, let the charge on the right electrode be Q . When the electron has passed from the left electrode (where x is equal to zero) to the point $x > 0$, this movement leads to the appearance of an induced charge on the electrodes. The charge on the right electrode is now equal to

$$Q(x) = Q - ex/d. \quad (3.3.7)$$

Here the minus sign is due to the negative charge of the electron. When the electron arrives at the right electrode, we have the charge $(Q - e)$ instead of Q . It is essential that the charge is independent of the velocity of the electron.

Substituting the charge (3.3.7) for the charge Q in (3.3.6) gives

$$f(x) = e \frac{d\varphi(x)}{dx} + \frac{eQ}{Cd} - \frac{e^2}{Cd^2} x. \quad (3.3.8)$$

The mechanical potential

$$U_1(x) = - \int_0^x f(x') dx' \equiv - e\varphi(x) - \frac{eQ}{Cd} x + \frac{e^2}{2Cd^2} x^2 \quad (3.3.9)$$

corresponds to this force field. If the electron moves from the right to the left, instead of (3.3.7) we will have

$$Q(x) = Q + e \frac{d-x}{d}, \quad (3.3.10)$$

and instead of (3.3.9) the potential will be

$$\begin{aligned} U_2(x) &= - \int_d^x f(x') dx' = \int_x^d f(y) dy \\ &= - e\varphi(x) + \frac{eQ}{Cd}(d-x) + \frac{e^2}{2Cd^2}(d-x)^2. \end{aligned} \quad (3.3.11)$$

In (3.3.9, 11) the integration paths correspond to the track of the electron and $\varphi(0) = \varphi(d) = 0$. Let the electrodes have a temperature T and let the electrons have the Maxwell velocity distribution. Therefore, the electrons have a range of energies. Only electrons that can overcome the maximum of the potential (3.3.9) can move between the electrodes from the left to the right. Other electrons must return. Only those electrons that can overcome the maximum of the potential (3.3.11) can move from the right to the left. The point of the maximum of potential (3.3.9) is denoted by x_1 , and the point of the maximum of (3.3.11) is denoted by x_2 . Equating the potential derivatives at these points to zero, we obtain the equations

$$\begin{aligned} -\varphi'(x_1) - \frac{Q}{Cd} + \frac{e}{Cd^2} x_1 &= 0, \\ -\varphi'(x_2) - \frac{Q}{Cd} - \frac{e}{Cd^2}(d-x_2) &= 0 \end{aligned} \quad (3.3.12)$$

which determine x_1 and x_2 .

The fraction of electrons crossing the potential barrier is determined by the expression $\exp[-\beta U_i(x_i)]$, $i = 1, 2$; $\beta^{-1} = kT$. Consequently, for the currents I_+ and I_- (I_+ is due to electron motion from the left to the right and I_- is due to electrons moving in the opposite direction) we have

$$I_+ = -I_0 \exp[-\beta U_1(x_1)], \quad (3.3.13a)$$

$$I_- = I_0 \exp[-\beta U_2(x_2)], \quad (3.3.13b)$$

where $I_0 > 0$ is a constant which has the dimensions of current. The total current $\dot{Q} = I$ is

$$I = I_+ + I_- = -I_0 \exp[-\beta U_1(x_1)] + I_0 \exp[-\beta U_2(x_2)]. \quad (3.3.14)$$

Inserting (3.3.9, 11) into this expression gives

$$\begin{aligned} \dot{Q} = I(Q) = & -I_0 \left\{ \exp \left[\beta e\varphi(x_1) + \beta \frac{eQ}{Cd} x_1 - \frac{\beta e^2}{2Cd^2} x_1^2 \right] \right. \\ & \left. - \exp \left[\beta e\varphi(x_2) - \beta \frac{eQ}{Cd} (d - x_2) - \frac{\beta e^2}{2Cd^2} (d - x_2)^2 \right] \right\}. \end{aligned} \quad (3.3.15)$$

To obtain a simpler explicit expression for the dependence $I(Q)$, we assume that $-e\varphi(x)$ has a sharp maximum, i.e. in the neighbourhood of the maximum point the following equation is valid:

$$-d^2\varphi(x)/dx^2 = (\sigma/\epsilon_0)\delta(x - x_0). \quad (3.3.16)$$

This means that the stable negative space charge is concentrated, with a surface density $\sigma < 0$, on the surface $x = x_0$. Hence, if the charge Q is not too large, the maximum points x_1 and x_2 determined by (3.3.12) coincide. They are independent of Q and equal to x_0 . Then (3.3.15) takes the form

$$\dot{Q} = I(Q) = -I_1 \left[\exp \left(\frac{\beta e p Q}{C} - \frac{\beta e^2 p^2}{2C} \right) - \exp \left(-\frac{\beta e q}{C} Q - \frac{\beta e^2 q^2}{2C} \right) \right], \quad (3.3.17)$$

where the notations used are:

$$p = x_0/d, \quad q = 1 - p, \quad I_1 = I_0 \exp[\beta e\varphi(x_0)]. \quad (3.3.18)$$

Equation (3.3.17) is the nonlinear relaxation equation for this system since it determines the charge relaxation.

3.3.3 Diode Model: Explanation of the Paradox Related to Detection of Thermal Fluctuations

We denote the current–voltage characteristic of the nonlinear resistor by the relation $I = f(V)$. Since $V = Q/C$, the relaxation equation can be written as

$$\dot{Q} = -f(Q/C). \quad (3.3.19)$$

Comparing (3.3.17) with (3.3.19), we obtain the expression for the current–voltage

characteristic of our model:

$$f(V) = I_1 \left[\exp\left(\beta e p V - \frac{\beta e^2 p^2}{2C}\right) - \exp\left(-\beta e q V - \frac{\beta e^2 q^2}{2C}\right) \right]. \quad (3.3.20)$$

If $p \neq q$, then this characteristic is nonsymmetrical. In this case the nonlinear resistor has unidirectional conduction. It is known that nonlinear resistors with unidirectional conduction (detectors) can detect, i.e. they can rectify the alternating voltage applied to them. But the fluctuational voltage is also an alternating one. The question arises of whether or not nonlinear resistors in a state of equilibrium can create a constant current or constant voltage by merely detecting the thermal fluctuations. According to the second law of thermodynamics, random thermal motion cannot create ordered motion. Therefore, the hypothetical phenomenon of thermal fluctuation detection contradicts the second law of thermodynamics and, consequently, is impossible.

Turning to the characteristic (3.3.20) calculated for our model precisely, we can easily verify that the detection of thermal fluctuations is impossible. The important point is that a new factor arises, which is not taken into account in the hypothetical fluctuation detection. Namely, the characteristic (3.3.20) is shifted in the vertical direction and does not pass through the origin of coordinates. In fact,

$$f(0) = I_1 \left[\exp\left(\frac{\beta e^2 p^3}{2C}\right) - \exp\left(-\frac{\beta e^2 q^2}{2C}\right) \right] \neq 0 \quad \text{for } p \neq q. \quad (3.3.21)$$

If there were no such shift, the mean current

$$\langle I \rangle = \int f(V) w_{eq}(V) dV \quad (3.3.22)$$

would differ from zero. If we now take into account the form of the equilibrium probability density

$$w_{eq}(V) = \text{const} \cdot \exp(-\beta C V^2 / 2) \quad (3.3.23)$$

and substitute (3.3.20, 23) into (3.3.22), after averaging we obtain $I = 0$. Thus, the second law of thermodynamics is not violated. The averaged characteristic

$$\bar{f}(U) = \int f(V) w_U(V) dV \quad (3.3.24)$$

must pass through the origin of coordinates. In the general case this is expressed by equation (4.1.10), which will be derived later. For the case under study the characteristic (3.3.24) is of the form

$$\bar{f}(U) = I_1 [\exp(\beta e p U) - \exp(-\beta e q U)]. \quad (3.3.25)$$

Thus, one should distinguish the precise characteristic of nonlinear elements from the averaged one. Of course, the difference between them is small (of the order of e or k), but has a vital influence when such a small effect as thermal fluctuation detection is considered.

3.3.4 Diode Model: The Kinetic Potential and Its Image

As has been shown in Sect. 3.3.2, I_+ is the current through the diode due to electron transitions from the left to the right. Each of these transitions decreases the charge Q by e , i.e. it corresponds to the jump $Q \rightarrow Q - e$. The duration of the transition is assumed to be negligible. Using (3.3.13a), we can readily find the mean number of jumps per unit time

$$\begin{aligned} n_+(Q) &= -I_+(Q)/e \\ &= (I_0/e)\exp[-\beta U_1(x_0)]. \end{aligned} \quad (3.3.26)$$

If there were no inverse transitions, the transitions $Q \rightarrow Q - e$ would imply the following rate of change of probability density $w(Q)$:

$$\partial w(Q)/\partial t = n_+(Q + e)w(Q + e) - n_+(Q)w(Q). \quad (3.3.27)$$

In fact, as a consequence of the jump $Q \rightarrow Q - e$ the values of $w(Q)$ are influenced by the values of $n_+(Q + e)w(Q + e)$, i.e. by the values at the point from where the jump is made to the point Q . In (3.3.27) the term $-n_+(Q)w(Q)$ describes the decrease of probability caused by the jumps from the point Q .

Considering the jumps $Q \rightarrow Q + e$, the frequency of which is equal to

$$\begin{aligned} n_-(Q) &= I_-(Q)/e \\ &= (I_0/e)\exp(-\beta U_2(x_0)), \end{aligned} \quad (3.3.28)$$

we add appropriate terms to (3.3.19) and finally obtain

$$\begin{aligned} \partial w(Q)/\partial t &= n_+(Q + e)w(Q + e) + n_-(Q - e)w(Q - e) \\ &\quad - [n_+(Q) + n_-(Q)]w(Q). \end{aligned} \quad (3.3.29)$$

Using a formula of the type (3.2.48), we can write this equation in the form

$$\begin{aligned} \partial w(Q)/\partial t &= [\exp(e\partial/\partial Q) - 1][n_+(Q)w(Q)] \\ &\quad + [\exp(-e\partial/\partial Q) - 1][n_-(Q)w(Q)]. \end{aligned} \quad (3.3.30)$$

Finally, substituting (3.3.26, 28) and also (3.3.9, 11) into (3.3.30), we find

$$\begin{aligned} \partial w(Q)/\partial t &= [\exp(e\partial/\partial Q) - 1][(I_1/e)\exp(\beta epQ/C - \beta e^2 p^2/2C)w(Q)] \\ &\quad + [\exp(-e\partial/\partial Q) - 1][(I_1/e)\exp(-\beta eqQ/C - \beta e^2 q^2/2C)w(Q)], \end{aligned} \quad (3.3.31)$$

where the notations (3.3.18) introduced earlier are used.

According to (2.3.24) linear components (in $\partial/\partial Q$) of the expansion of the right-hand side of (3.3.31) in terms of $\partial/\partial Q$ must have the form $-(\partial/\partial Q) K_1(Q)w(Q)$. Selecting these components, we have

$$K_1(Q) = I(Q), \quad (3.3.32)$$

where $I(Q)$ is defined by (3.3.17). Thus, the function $I(Q)$ obtained previously is simply the first coefficient function $K_1(Q)$.

Comparing the master equation (3.3.31) with (3.1.11), we find the kinetic potential corresponding to the diode model

$$\begin{aligned} V(y, Q) = \frac{I_1}{\beta e} & \left\{ [\exp(-\beta ey) - 1] \exp\left(\frac{\beta epQ}{C} - \frac{\beta e^2 p^2}{2C}\right) \right. \\ & \left. + [\exp(\beta ey) - 1] \exp\left(-\frac{\beta eqQ}{C} - \frac{\beta e^2 q^2}{2C}\right) \right\}. \end{aligned} \quad (3.3.33)$$

According to (3.1.32), we can now find the image $R(y, x)$. In (3.1.32) the probability density $w_x(B)$ is defined by (3.1.29), i.e. in our case by

$$w_x(Q) = \text{const} \cdot \exp(\beta x Q) w_{\text{eq}}(Q). \quad (3.3.34)$$

Here x has the meaning of an external e.m.f. We shall write U instead of x . Using the formula $w_{\text{eq}}(Q) = \text{const} \cdot \exp[-W(Q)]$ at $W(Q) = Q^2/2C$, we obtain the equilibrium probability density

$$w_{\text{eq}}(Q) = (2\pi C/\beta)^{-1/2} \exp(-\beta Q^2/2C). \quad (3.3.35)$$

Hence, the probability density (3.3.34) takes the form

$$w_U(Q) = (2\pi k T C)^{-1/2} \exp[-(\beta/2C)(Q - CU)^2]. \quad (3.3.36)$$

Averaging (3.3.33) with the weight (3.3.36), we obtain the image

$$\begin{aligned} R(y, U) = [I_1/(\beta e)] & \{ [\exp(-\beta ey) - 1] \exp(\beta e p U) \\ & + [\exp(\beta ey) - 1] \exp(-\beta e q U) \}. \end{aligned} \quad (3.3.37)$$

We easily verify that this function satisfies the generating equation (3.2.50), which, as a consequence of the time evenness ($\varepsilon_1 = 1$) of charge, has the form

$$R(y + U, U) = R(-y, U). \quad (3.3.38)$$

Substituting (3.3.37) into (3.3.38) and taking into account the equation $1 - p = q$, we make sure of the validity of the last equation.

In conclusion we note that, applying (3.1.41) to (3.3.37), we readily find the image of the first coefficient function

$$\kappa_1(U) = -I_1[\exp(\beta e p U) - \exp(-\beta e q U)]. \quad (3.3.39)$$

It coincides, except in sign, with the averaged characteristic (3.3.25). Therefore, the condition of the absence of thermal fluctuation detection, which is fulfilled in this case, can be written as $\kappa_1(0) = 0$.

3.3.5 Poisson Model of Nonlinear Resistor: Construction of the Markov Operator Using Current–Voltage Characteristics

We now consider the more general model, namely, the Poisson model, in which no specific mechanism of charge carrier transfer is assumed and an arbitrary dependence of the number of jumps n_+ and n_- on the voltage V is allowed. In this model we suppose that in the resistor a relatively thin layer (junction or transition) is the

only main obstacle to the motion of the charge carriers. We also suppose that in both directions charge is transferred by the definite portions and that the instants of their transfer may be regarded as statistically independent, i.e. the charge transfer through the layer in both directions may be treated as a Poisson process. This model can be applied to p–n-transitions, to the Schottky and tunnel diodes. For the sake of generality we will assume that the charge $\pm ye$ is transferred in a single event. A deviation of γ from unity is observed in the experiments [3.2]. For the Poisson model, (3.3.30) takes the form

$$\begin{aligned} \frac{\partial w(Q)}{\partial t} = & [\exp(\gamma e \partial / \partial Q) - 1] [n_+(V(Q))w] \\ & + [\exp(-\gamma e \partial / \partial Q) - 1] [n_-(V(Q))w] . \end{aligned} \quad (3.3.40)$$

The kinetic potential

$$V(y, Q) = kT \{ [\exp(-\beta\gamma ey) - 1] n_+(V(Q)) + [\exp(\beta\gamma ey) - 1] n_-(V(Q)) \} \quad (3.3.41)$$

corresponds to (3.3.40). Turning to the image (3.1.32) this gives

$$R(y, V) = kT \{ [\exp(-\beta\gamma ey) - 1] \bar{n}_+(V) + [\exp(\beta\gamma ey) - 1] \bar{n}_-(V) \} , \quad (3.3.42)$$

where

$$\bar{n}_\pm(V) = \int n_\pm(V(Q)) w_V(Q) dQ \approx n_\pm(V) . \quad (3.3.43)$$

Assuming a small error of order kT , we can neglect the difference between $\bar{n}_\pm(V)$ and $n_\pm(V)$.

The image (3.3.42) must satisfy the generating equation $R(y + V, V) = R(-y, V)$, i.e. equation (3.3.38) in which U is replaced by V . Substituting (3.3.42) into this generating equation, after cancellations we obtain

$$(e^{-by} - e^{by + \beta V})(e^{-bV} n_+ - n_-) = 0 \quad (b = \beta\gamma e) . \quad (3.3.44)$$

Owing to the arbitrariness of y , we then find

$$n_-(V) = \exp(-\beta\gamma e V) n_+(V) . \quad (3.3.45)$$

Using this equation, we can easily construct the Markov operator if we know the current–voltage characteristic, which is determined by the drift coefficient $K_1(Q)$ corresponding to the master equation (3.3.40). We readily get

$$K_1(Q) = -\gamma e [n_+(V(Q)) - n_-(V(Q))] . \quad (3.3.46)$$

If we neglect the fluctuations, the evolution equation assumes the form $\dot{Q} = K_1(Q)$, i.e.

$$I = -\gamma e [n_+(V(Q)) - n_-(V(Q))] = -f(V(Q)) . \quad (3.3.47)$$

Consequently, the current–voltage characteristic is of the form

$$f(V) = \gamma e [n_+(V) - n_-(V)] . \quad (3.3.48)$$

Substituting (3.3.45) into (3.3.48) yields

$$\gamma e [1 - \exp(-\beta \gamma e V)] n_+(V) = f(V). \quad (3.3.49)$$

Therefore,

$$\begin{aligned} n_+(V) &= (\gamma e)^{-1} [1 - \exp(-\beta \gamma e V)]^{-1} f(V), \\ n_-(V) &= (\gamma e)^{-1} [\exp(\beta \gamma e V) - 1]^{-1} f(V). \end{aligned} \quad (3.3.50)$$

The substitution of (3.3.50) into (3.3.40) solves the problem of constructing the kinetic operator.

It should be noted that (3.3.40) is valid not only when the nonlinear resistor is connected with a capacitor as is shown in Fig. 3.1, but also when the capacitor is absent and the voltage of the voltage source with negligible internal resistance is applied across the nonlinear resistor (Fig. 3.4). In this case the coefficients of the master equation are independent of Q . Transforming (3.3.40) to the form (2.3.24), we easily find

$$K_n(V) = (\gamma e)^n [n_-(V) + (-1)^n n_+(V)]. \quad (3.3.51)$$

Substituting (3.3.50) into (3.3.51) gives

$$\begin{aligned} K_n(V) &= (\gamma e)^n \coth(\frac{1}{2}\beta \gamma e V) f(v) && \text{for even } n, \\ K_n(V) &= -(\gamma e)^{n-1} f(v) && \text{for odd } n. \end{aligned} \quad (3.3.52)$$

In particular,

$$K_2(V) = \gamma e \coth(\frac{1}{2}\beta \gamma e V) f(V). \quad (3.3.53)$$

From

$$\begin{aligned} K_2 &= \lim_{\tau \rightarrow 0} \tau^{-1} \langle \Delta Q^2 \rangle \\ &= \lim_{\tau \rightarrow 0} \tau^{-1} \int_0^\tau \int_0^\tau \langle J(t)J(t') \rangle dt dt' \end{aligned} \quad (3.3.54)$$

we have

$$\begin{aligned} \langle J(t)J(t') \rangle &= K_2 \delta(t - t'), \\ S_J &\equiv \int \exp(i\omega(t - t')) \langle J(t)J(t') \rangle d(t - t') = K_2. \end{aligned} \quad (3.3.55)$$

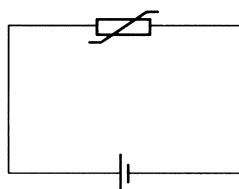


Fig. 3.4. Simple electric circuit with nonlinear resistor and voltage source

Therefore, (3.3.53) gives

$$S_\xi = S_J = \gamma e \coth(\frac{1}{2}\beta\gamma e V) f(V). \quad (3.3.56)$$

This formula (for $\gamma = 1$) is well known [3.3, 4].

3.3.6 Gupta's Formulas

In [3.5] *Gupta* derived the following formulas for the spectral densities of the current I in the nonlinear resistor and of the voltage V across it:

$$S_I = 2kT[dI/dV - \frac{1}{2}I d^2 I/dV^2(dI/dV)^{-1}], \quad (3.3.57)$$

$$S_V = 2kT[dV/dI + \frac{1}{2}I d^2 V/dI^2]. \quad (3.3.58)$$

Here the relation between I and V corresponds to the current–voltage characteristic. However, these formulas cannot be regarded as well-founded; therefore, they have considerably less generality and significance than (3.3.56).

We now touch on the derivation of (3.3.57) in [3.5]. In this work two conjugate thermodynamic parameters α and β are considered, α being the internal parameter and β the external one (the value $\beta = 0$ corresponds to equilibrium). The external parameter or the thermodynamic force is assumed to be equal to the sum $\beta(t) = \beta_0 + \Delta\beta(t)$ of the constant shift β_0 corresponding to the nonequilibrium steady state and a small addition $\Delta\beta(t)$, which is switched on at a certain moment of time; for example,

$$\Delta\beta(t) = \begin{cases} c \sin vt & \text{for } t > t_0, \\ 0 & \text{for } t < t_0. \end{cases} \quad (3.3.59)$$

The author of [3.5] related the dissipated power $-\langle \dot{F} \rangle = \langle \dot{\alpha}(t)\beta(t) \rangle$ to derivatives (with respect to time) of the correlation function $\langle \alpha(t), \alpha(t+\tau) \rangle$. This was achieved by using the formula relating the linear response $\delta\langle \alpha(t) \rangle / \delta\Delta\beta(t')$ to the correlation function $\langle \alpha(t), \alpha(t+\tau) \rangle$. Namely, in deriving formula (29) of the work [3.5], which was valid in the approximation linear in deviations from equilibrium, Gupta gave no foundation for generalizing this formula to nonlinear region. It is known that there is no general formula connecting the linear response taken at nonequilibrium steady state with the correlation functions of the internal parameter at this state. Therefore, it is no wonder that Gupta's formulas are not always valid [3.6].

Let us verify the validity of (3.3.57) in the case of the diode model when (3.3.31) is valid. If we go over from the circuit in Fig. 3.1 to the circuit given in Fig. 3.4, instead of (3.3.31), we shall have

$$\begin{aligned} \frac{\partial w(Q)}{\partial t} = \frac{I}{e} & \left\{ \left[\exp\left(e \frac{\partial}{\partial Q}\right) - 1 \right] [\exp(\beta e p V) w] \right. \\ & \left. + \left[\exp\left(-e \frac{\partial}{\partial Q}\right) - 1 \right] [\exp(-\beta e q V) w] \right\}. \end{aligned} \quad (3.3.60)$$

Here we have replaced Q/C by V ; the small terms containing βe^2 have been

omitted. Hence, we easily find the diffusion coefficient

$$K_2 = eI_1[\exp(\beta epV) + \exp(-\beta eqV)] . \quad (3.3.61)$$

Consequently, by virtue of (3.3.55), we get

$$S_I(V) = eI_1[\exp(\beta epV) + \exp(-\beta eqV)] . \quad (3.3.62)$$

Using this equation and the current-voltage characteristic (3.3.25), i.e.

$$I(V) = \bar{f}(V) = I_1[\exp(\beta epV) - \exp(-\beta eqV)] , \quad (3.3.63)$$

we can easily check the validity of (3.3.57) by direct substitution. After cancellations and some algebra this substitution gives the equation $p(1 - p) = 0$. Therefore, for the diode model Gupta's formula is valid only for $p = 0$ and $p = 1$.

We now put aside the diode model and consider the tunnel diode model with current-voltage characteristic

$$I = f(V) = Ae^{-aV} + B(e^{bV} - 1) , \quad (3.3.64)$$

where A, B, a, b are constants. Applying (3.3.56) at $\gamma = 1$ gives

$$S_I = e \coth(\frac{1}{2}\beta eV)[Ae^{-aV} + B(e^{bV} - 1)] . \quad (3.3.65)$$

Substituting (3.3.64, 65) into (3.3.57), we see that Gupta's formula does not hold in this case.

Let us now consider Gupta's formula (3.3.58). In [3.5] the following derivation of this formula was given. Owing to the smallness of the fluctuational current $I_f = I - \langle I \rangle$, we have

$$V - \langle V \rangle = \frac{dV}{dI} I_f = \left(\frac{dI}{dV} \right)^{-1} I_f . \quad (3.3.66)$$

Here the terms of order I_f^2 and higher are omitted. Hence, we get

$$S_V = \left(\frac{dI}{dV} \right)^{-2} S_I . \quad (3.3.67)$$

If we substitute (3.3.57) into the right-hand side of this equation, we obtain (3.3.58). This derivation of (3.3.58) is beneath criticism. The fact is that the dependence $I(V)$ entering into (3.3.57) is the dependence of the average current on the unfluctuational part of voltage. Here the fluctuational current is not taken into account. An entirely different dependence $I(V)$ – that of the fluctuational current on fluctuational voltage – must enter into (3.3.66, 67). To avoid the possibility of errors similar to the one committed in deriving (3.3.67), one should write S_J and S_U on the left-hand sides of (3.3.57, 58), where J and U are the total current and voltage including their fluctuational parts. The average current $I = \langle J \rangle$ and voltage $V = \langle U \rangle$ appear on the right-hand sides of (3.3.57, 58).

In reality, (3.3.58) does not hold when (3.3.57) is valid: for instance, in the diode model at $p = 1$ and in the case of the circuit shown in Fig. 3.4 when (3.3.57) is valid. In this case the fluctuations of voltage are absent since the voltage source has zero internal resistance, i.e. (3.3.58) is wrong.

However, (3.3.58) can be valid sometimes. To demonstrate this we consider the more complex circuit containing an additional capacitance C and a linear resistance R_1 (Fig. 3.5). The mean constant currents I , I_1 and the mean voltage V across the capacitance can be worked out by using the equations

$$I = I_1, \quad f(I) + R_1 I = \mathcal{E}, \quad V = f(I). \quad (3.3.68)$$

Here \mathcal{E} is the power supply voltage. We now calculate the fluctuational components of the currents, $I_f = J - I$, $i_1 = J_1 - I_1$, and the fluctuational voltage $v = U - V$ across the capacitance. The circuit being considered has two sources of fluctuations: shot fluctuations of the current arising in the nonlinear resistor (it is assumed that the diode model of this resistor can be applied) and a thermal fluctuational e.m.f. arising in R_1 . It is convenient to use the equivalent circuit given in Fig. 3.6 for calculating the contribution of shot fluctuations to fluctuations of voltage and current. We see that the following equations are valid:

$$\begin{aligned} R_d i &= (i\omega C)^{-1} i_2 = R_1 i_1 = v, \\ i + i_2 + i_1 &= \tilde{J}_f, \end{aligned} \quad (3.3.69)$$

where $R_d = f'(I)$ is the differential resistance of the nonlinear resistor; i is the current through R_d in the equivalent circuit (the real fluctuational current through the nonlinear resistor is equal to $J_f = \tilde{J}_f - i$); \tilde{J}_f is the shot noise current having the spectral density

$$\tilde{S}_J(V) = eI_1(e^{\beta eV} + 1) \quad (3.3.70)$$

obtained from (3.3.62) at $p = 1$. Solving equations (3.3.69) gives

$$\begin{aligned} i &= R_d^{-1} (i\omega C + R_d^{-1} + R_1^{-1})^{-1} \tilde{J}_f, \\ v &= (i\omega C + R_d^{-1} + R_1^{-1})^{-1} \tilde{J}_f, \\ J_f &= (i\omega C R_1 + 1) (i\omega C R_1 + R_1/R_d + 1)^{-1} \tilde{J}_f, \end{aligned} \quad (3.3.71)$$

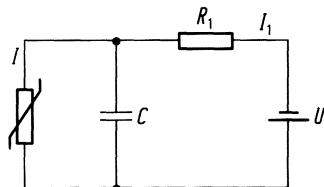


Fig. 3.5. More complex circuit with linear resistor

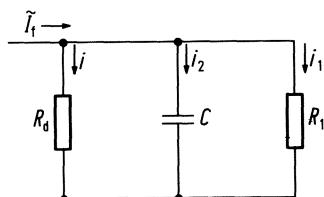


Fig. 3.6. Equivalent circuit for calculating the shot-noise part of the voltage and current fluctuations

and, therefore,

$$S_U = \frac{R_1^2}{\omega^2 C^2 R_1^2 + m^2} eI_1(e^{\beta eV} + 1), \quad (3.3.72a)$$

$$S_J = \frac{\omega^2 C^2 R_1^2 + 1}{\omega^2 C^2 R_1^2 + m^2} eI_1(e^{\beta eV} + 1), \quad (3.3.72b)$$

where $m = 1 + R_1/R_d$. For calculating the contribution of the thermal fluctuational e.m.f. arising in R_1 we must consider another equivalent circuit (Fig. 3.7). In this case we have

$$v = \frac{(i\omega C + R_d^{-1})^{-1}}{R_1 + (i\omega C + R_d^{-1})^{-1}} \xi, \quad J_f = v/R_d, \quad (3.3.73)$$

where ξ is the noise e.m.f. with spectral density

$$S_\xi = 2kT R_1 \quad (3.3.74)$$

(the Nyquist formula). Finding the contribution of the e.m.f. due to thermal noise to S_U and S_J by using (3.3.73, 74) and adding this contribution to (3.3.72), we finally arrive at

$$S_U = (\omega^2 C^2 R_1^2 + m^2)^{-1} [R_1^2 eI_1(e^{\beta eV} + 1) + 2kT R_1], \quad (3.3.75a)$$

$$S_J = (\omega^2 C^2 R_1^2 + m^2)^{-1} [(\omega^2 C^2 R_1^2 + 1)eI_1(e^{\beta eV} + 1) + 2kT R_1/R_d^2]. \quad (3.3.75b)$$

We see that these spectral densities are not connected by (3.3.67). Therefore, Gupta's formulas (3.3.57, 58) are never applied to the same circuit simultaneously (for our example). If in (3.3.75a) we put $C = 0$ and let R_1 tend to infinity, we obtain

$$\begin{aligned} S_U &= R_d^2 eI_1(e^{\beta eV} + 1) \\ &= (I_1 \beta e)^{-2} \exp(-2\beta eV) eI_1[\exp(\beta eV) + 1]. \end{aligned} \quad (3.3.76)$$

It is easy to verify that this spectral density satisfies (3.3.58) when the current-voltage characteristic has the form: $I(V) = I_1(e^{\beta eV} - 1)$; [see (3.3.63)]. In this case the equation $S_J = 0$ is valid instead of (3.3.57). Thus, there is a certain narrow region of validity of (3.3.58).

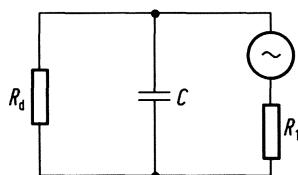


Fig. 3.7. Equivalent circuit for calculating the thermal-noise part of fluctuations

3.4 Other Examples: Chemical Reactions and Diffusion

3.4.1 Chemical Reactions and Reaction Equations

As an example we consider the reaction between gaseous I_2 (iodine) and H_2 (hydrogen). We suppose here that the following reactions proceed simultaneously:



Here the reaction rate constants are given above or below the arrows; they show the reaction rates in each direction. We will denote the molar concentrations (i.e. the number of moles per unit volume) of molecules and atoms by $[I_2]$, $[I]$, etc. The equations

$$\begin{aligned} d[I_2]/dt &= -k_1[I_2] + k_{-1}[I]^2, \\ d[I]/dt &= 2k_1[I_2] - 2k_{-1}[I]^2 - 2k_2[I]^2[H_2] + 2k_{-2}[HI]^2, \\ d[HI]/dt &= -2d[H_2]/dt = 2k_2[I]^2[H_2] - 2k_{-2}[HI]^2 \end{aligned} \quad (3.4.2)$$

correspond to reactions (3.4.1). Let us also introduce the following notation: we denote by E_1, \dots, E_r the chemical symbols of molecules, atoms and ions that take part in reactions. Here r is the total number of simultaneously reacting types of particles. In the above example $r = 4$; we can write E_1, E_2, E_3, E_4 instead of I_2, I, H_2, HI . Let s be the number of reactions going on simultaneously. The reaction equations have the form

$$\sum_{j=1}^r v'_{ij} E_j \xrightleftharpoons[k_{-i}]{k_i} \sum_{j=1}^r v_{ij} E_j, \quad i = 1, \dots, s, \quad (3.4.3)$$

where v_{ij} and v'_{ij} are nonnegative integers. The first subscript of the matrices v_{ij} and v'_{ij} denotes the reaction number and the second one denotes the substance number, i.e. the type of particles. For the above example we have

$$v'_{11} = 1, \quad v'_{22} = 2, \quad v'_{23} = 1, \quad v_{12} = 2, \quad v_{24} = 2. \quad (3.4.4)$$

The other coefficients are equal to zero. Cases are possible (for instance, in the presence of a catalyst) where molecules of the same type appear on both sides of (3.4.3) for the same reaction. For this reason, in the general case it is not advisable to transpose all terms of (3.4.3) to the right-hand side and to use the coefficients $\bar{v}_{ij} = v_{ij} - v'_{ij}$, which can be negative. The molar concentrations of E_j are also denoted by c_j . The equations for the concentrations

$$dc_j/dt = \sum_{i=1}^s (v_{ij} - v'_{ij}) \left[k_i \prod_{l=1}^r c_l^{v_{il}} - k_{-i} \prod_{l=1}^r c_l^{v'_{il}} \right] \quad (3.4.5)$$

correspond to general reactions (3.4.3). The sum and products on the right-hand side of (3.4.5) have only a few terms and cofactors since many of the matrix elements v_{ij} and v'_{ij} are equal to zero. This is seen from the above example, for which equations (3.4.5) are of the form (3.4.2).

For the chemical equilibrium when all derivatives dc_j/dt are equal to zero, (3.4.5) yields

$$\sum_{i=1}^s (v_{ij} - v'_{ij}) \left(k_i \prod_{l=1}^r c^{v'_{il}} - k_{-i} \prod_{l=1}^r c^{v_{il}} \right) = 0, \quad j = 1, \dots, r. \quad (3.4.6)$$

It should be noted that the principle of detailed balance requires the fulfilment of the stricter equations

$$\prod_{l=1}^r c_l^{v_{il}} - c_l^{v'_{il}} = k_i/k_{-i}, \quad i = 1, \dots, s \quad (3.4.7)$$

at $c_l = c_l^0$, where c_l^0 are the equilibrium values of c_l .

In the case (3.4.2) we find that the equilibrium concentrations must satisfy the equations

$$[I]^2/[I_2] = k_1/k_{-1}, \quad [HI]^2 [I]^{-2} [H_2]^{-1} = k_2/k_{-2}. \quad (3.4.8)$$

In our example, (3.4.8) follows from equations of the type (3.4.6); however, this is not always the case.

The reactions (3.4.1) are taken only as an example; it is of no importance for us how the reaction between H_2 and I_2 occurs in reality. If instead of (3.4.1) the one-step reaction



takes place, we find, instead of (3.4.2),

$$\begin{aligned} d[I_2]/dt &= d[H_2]/dt = -k'_1 [I_2] [H_2] + k'_{-1} [HI]^2, \\ d[HI]/dt &= 2k'_1 [I_2] [H_2] - 2k'_{-1} [HI]^2. \end{aligned} \quad (3.4.10)$$

Here $s = 1$, $v'_{11} = 1$, $v'_{12} = 1$, $v_{13} = 2$, and the condition of equilibrium has the form

$$[HI]^2 [I_2]^{-1} [H_2]^{-1} = k'_1/k'_{-1}. \quad (3.4.11)$$

A condition of a similar type is fulfilled also for reactions (3.4.1). In fact, taking into account that the product of the left-hand sides of (3.4.8) is equal to the product of their right-hand sides, we obtain

$$[HI]^2 [I_2]^{-1} [H_2]^{-1} = k_1 k_2 / (k_{-1} k_{-2}). \quad (3.4.12)$$

This equation coincides with (3.4.11) if $k'_1/k'_{-1} = k_1 k_2 / (k_{-1} k_{-2})$.

3.4.2 Chemical Potentials

Let us denote the number of moles of a substance E_i in the volume V by $C_i = c_i V$. The mole numbers C_1, \dots, C_r are a special case of the internal thermodynamic parameters $A_j = B_j(z)$. We define the external thermodynamic parameters μ_j

conjugate to C_j by (3.1.47), i.e. by

$$\mu_j = \partial F_0(T, C) / \partial C_j, \quad j = 1, \dots, r. \quad (3.4.13)$$

These parameters are called the chemical potentials of the substances E_j .

In (3.4.13) $F_0(T, C)$ is the free energy, for which the first law of thermodynamics takes the form (3.1.48), namely,

$$dF_0(T, C) = -S dT + \sum_{j=1}^r \mu_j dC_j. \quad (3.4.14)$$

If the volume V of the system can also vary in addition to C_j and T , one should write an additional term in (3.4.14). After that we have

$$dF_0(T, V, C) = -S dT - p dV + \sum_{j=1}^r \mu_j(T, V, C) dC_j. \quad (3.4.15)$$

Hence,

$$p(T, V, C) = -\partial F_0(T, V, C) / \partial V. \quad (3.4.16)$$

Using (3.4.13, 16) gives

$$\partial \mu_j(T, V, C) / \partial V = -\partial p(T, V, C) / \partial C_j. \quad (3.4.17)$$

This equation can be used to determine the dependence $\mu_j(T, V, C)$. We assume that the substances E_1, \dots, E_r are ideal gases. Consequently, the pressure p is determined by the ideal gas equation

$$p = \sum_{j=1}^r C_j RT / V. \quad (3.4.18)$$

External forces are assumed absent and for this reason the gas is homogeneous in space. The various components of the ideal gas do not interact mechanically and, therefore, the chemical potential of the i th gas must depend only on the number of the moles C_i of this gas and it must be independent of the quantity of other components. We now take a subvolume $V^{(1)}$ of the volume V , say, $V^{(1)} = V/10$. Then the free energy $F_0^{(1)}$ of the subvolume is ten times smaller than the total free energy $F_0(T, V, C)$, but the derivative $\partial F_0^{(1)} / \partial C_j^{(1)}$ for the subvolume is equal to the derivative $\partial F_0 / \partial C_j$ for V . This means that the chemical potential (3.4.13) has a local character, i.e. it is an intensive parameter. It does not separately depend on C_i and V , but only on the ratio C_i/V :

$$\mu_j(T, V, C_j) = f_j(T, C_j/V). \quad (3.4.19)$$

Substituting (3.4.18, 19) into (3.4.17) gives

$$-\frac{\partial f(T, c_j)}{\partial c_j} \frac{C_j}{V^2} = -\frac{RT}{V}, \quad (3.4.20)$$

i.e.

$$\partial f(T, c_j) / \partial c_j = RT/c_j. \quad (3.4.21)$$

Integrating this equation one can find the form of the function $f(T, c_i)$ (to within an

additive constant) and, consequently, the form of the chemical potential

$$\mu_j(T, V, C_j) = \zeta_j(T) + RT \ln(C_j/V). \quad (3.4.22)$$

Here the constant $\zeta_i(T)$ is a characteristic of the substance E_i . It depends on the free energy of one particle of this substance.

The nonequilibrium values of μ_j and C_j are connected by (3.4.22). The equilibrium values μ_j^0 and C_j^0 are related by the same relation

$$\mu_j^0 = \zeta_j(T) + RT \ln(C_j^0/V). \quad (3.4.23)$$

According to (3.1.46), we have

$$\mu_j = \mu_j^0 + x_j, \quad (3.4.24)$$

where x_j are the thermodynamic forces conjugate to C_j . Using (3.4.22–24) we can obtain

$$x_j = RT \ln(C_j/C_j^0). \quad (3.4.25)$$

In (3.4.13, 14) the Gibbs free energy $G(T, p, C)$ can be taken as $F_0(T, C)$.

3.4.3 The Kinetic Potential Corresponding to (3.4.5)

According to (3.4.5), the rate of change of the mole number C_j induced by the i th reaction is equal to

$$dC_j^{(i)}/dt = (v_{ij} - v'_{ij}) V \left[k_i \prod_l (C_l/V)^{v'_{il}} - k_{-i} \prod_l (C_l/V)^{v_{il}} \right]. \quad (3.4.26)$$

We will regard $C_j(t)$ as a Markov fluctuational process. The number $N_j(t)$ of molecules of the substance E_j is changed stepwise for the i th reaction. For the i th forward reaction (3.4.3) jumps of the type $N_j \rightarrow N_j + v_{ij} - v'_{ij}$ occur. A single jump changes the mole number C_j in the following way: $C_{ij} \rightarrow C_j + (v_{ij} - v'_{ij})/N_A$, where N_A is Avogadro's number. Taking into account the term with k_i in (3.4.26), we can obtain the frequency n_i^+ of these jumps:

$$n_i^+(C) = N_A V k_i \prod_l (C_l/V)^{v'_{il}}. \quad (3.4.27)$$

If we had only the jumps corresponding to the substance E_j and only one reaction, the master equation would be of the form

$$\partial w(C)/\partial t = n_i^+ [C_j - (v_{ij} - v'_{ij})/N_A] w[C_j - (v_{ij} - v'_{ij})/N_A] - n_i^+(C) w(C) \quad (3.4.28)$$

or

$$\frac{\partial w(C)}{\partial t} = \left[\exp \left(- \frac{v_{ij} - v'_{ij}}{N_A} \frac{\partial}{\partial C_j} \right) - 1 \right] n_i^+(C) w(C). \quad (3.4.29)$$

Now we consider that for an elementary act of the molecule transformation the following simultaneous jumps:

$$C_1 \rightarrow C_1 + (v_{i1} - v'_{i1})/N_A, \dots, C_r \rightarrow C_r + (v_{ir} - v'_{ir})/N_A \quad (3.4.30)$$

occur in the i th reaction. Because there is a simultaneous change of various C_j , instead of (3.4.29) corresponding to one substance, we have

$$\frac{\partial w(C)}{\partial t} = \left[\exp\left(- \sum_j \frac{v_{ij} - v'_{ij}}{N_A} \frac{\partial}{\partial C_j} \right) - 1 \right] [n_i^+(Q) w(Q)], \quad (3.4.31)$$

where the summation now occurs under the exponent sign unlike in (3.4.29). The backward i th reaction leads to jumps $C_j \rightarrow C_j - (v_{ij} - v'_{ij})/N_A$, whose frequency is equal to

$$n_i^-(C) = N_A V k_{-i} \prod_l (C_l/V)^{v_{il}}. \quad (3.4.32)$$

These jumps also take place simultaneously, and correspond to the equation

$$\frac{\partial w(C)}{\partial t} = \left[\exp\left(- \sum_j \frac{v_{ij} - v'_{ij}}{N_A} \frac{\partial}{\partial C_j} \right) - 1 \right] [n_i^-(C) w(C)]. \quad (3.4.33)$$

Combining (3.4.31) and (3.4.33), summing over i , i.e. over the various reactions, and using (3.4.27, 32), we find the total master equation

$$\begin{aligned} \frac{\partial w(C)}{\partial t} = N_A V \sum_i & \left\{ \left[\exp\left(- \sum_j \frac{v_{ij} - v'_{ij}}{N_A} \frac{\partial}{\partial C_j} \right) - 1 \right] \right. \\ & \times \left[k_i \prod_l \left(\frac{C_l}{V} \right)^{v'_{il}} w(C) \right] + \left[\exp\left(\sum_j \frac{v_{ij} - v'_{ij}}{N_A} \frac{\partial}{\partial C_j} \right) - 1 \right] \\ & \left. \times \left[k_{-i} \prod_l \left(\frac{C_l}{V} \right)^{v_{il}} w(C) \right] \right\}. \end{aligned} \quad (3.4.34)$$

Comparing (3.4.34) with (3.1.11), we can easily obtain the kinetic potential

$$\begin{aligned} V(y, C) = RTV \sum_i & \left\{ \left[\exp\left(\sum_j \frac{v_{ij} - v'_{ij}}{RT} y_j \right) - 1 \right] k_i \prod_l \left(\frac{C_l}{V} \right)^{v'_{il}} \right. \\ & \left. + \left[\exp\left(- \sum_j \frac{v_{ij} - v'_{ij}}{RT} y_j \right) - 1 \right] k_{-i} \prod_l \left(\frac{C_l}{V} \right)^{v_{il}} \right\}. \end{aligned} \quad (3.4.35)$$

We now find the image (3.1.32) for the present case. However, unlike Sect. 3.3.4, we will carry out a less precise consideration, namely, we will use (3.1.37) and neglect the small terms of order k . Consequently, we have

$$R(y, x) = V(y, C(x)). \quad (3.4.36)$$

Using (3.4.25, 35), from (3.4.36) we obtain

$$\begin{aligned} R(y, x) = RTV \sum_i & \left\{ \left[\exp\left(\alpha \sum_j (v_{ij} - v'_{ij}) y_j \right) - 1 \right] k'_i \right. \\ & \times \exp\left(\alpha \sum_l v'_{il} x_l \right) + \left[\exp\left(- \alpha \sum_j (v_{ij} - v'_{ij}) y_j \right) - 1 \right] k'_{-i} \\ & \left. \times \exp\left(\alpha \sum_l v_{il} x_l \right) \right\}, \end{aligned} \quad (3.4.37)$$

where

$$\alpha = (RT)^{-1}, \quad k'_i = k_i \prod_l (c_l^0)^{v'_{il}}, \quad k'_{-i} = k_{-i} \prod_l (c_l^0)^{v_{il}}. \quad (3.4.38)$$

Let us now verify the fulfilment of the generating equation (3.2.50) for $R(y, x)$. Since all variables C_j are even in time, (3.2.50) takes the form

$$R(y + x, x) = R(-y, x), \quad (3.4.39)$$

By virtue of (3.4.37) the last equation gives

$$\sum_{i=1}^s \left[\exp \left(\sum_j \frac{v_{ij} - v'_{ij}}{RT} y_j + \sum_j \frac{v_{ij}}{RT} x_j \right) - \exp \left(- \sum_j \frac{v_{ij} - v'_{ij}}{RT} y_j + \sum_j \frac{v'_{ij}}{RT} x_j \right) \right] (k'_i - k'_{-i}) = 0. \quad (3.4.40)$$

This equation must be satisfied for all y and x . In many cases (3.4.40) implies the equations

$$k'_i = k'_{-i}. \quad (3.4.41)$$

If we set $x = 0$ in (3.4.40) and differentiate this equation with respect to y_i at point $y = 0$, we get

$$\sum_i (v_{ij} - v'_{ij}) (k'_i - k'_{-i}) = 0, \quad j = 1, \dots, r. \quad (3.4.42)$$

It is easily seen that (3.4.42) is equivalent to (3.4.6). If the rank of the matrix $v_{ij} - v'_{ij}$ is less than s and (3.4.42) is, therefore, insufficient for proving (3.4.41), we can obtain the set of equations by equating the vectors x, y in (3.4.40) to different pairs of vectors $x^{(1)}, y^{(1)}, \dots, x^{(s)}, y^{(s)}$. Sometimes, the new set of equations will be sufficient for proving (3.4.41), i.e. (3.4.7).

3.4.4 Extent of Reaction and the Corresponding Kinetic Potential

If the number of simultaneous reactions is less than the number of reagents, it is useful to introduce degrees of advancement or extents of reaction $\xi_i, i = 1, \dots, s$. They are defined by

$$dC_j = \sum_{i=1}^s (v_{ij} - v'_{ij}) d\xi_i. \quad (3.4.43)$$

To be definite we suppose that some values C_1^1, \dots, C_r^1 of mole numbers correspond to values $\xi_1 = 0, \dots, \xi_s = 0$. Then, in accordance with (3.4.43), we have

$$C_j(\xi) = C_j^1 + \sum_{i=1}^s (v_{ij} - v'_{ij}) \xi_i \quad (3.4.44)$$

If we substitute (3.4.43) into (3.4.15), we obtain

$$dF(T, V, \xi) = -S dT - p dV + \sum_{i,j} \mu_i (v_{ij} - v'_{ij}) d\xi_i . \quad (3.4.45)$$

The external parameters conjugate to ξ_i are defined by

$$\mathcal{A}_i = \partial F(T, V, \xi) / d\xi_i . \quad (3.4.46)$$

They are called the affinities. Using (3.4.45) we find how the affinities are expressed in terms of chemical potentials:

$$\mathcal{A}_i = \sum_j (v_{ij} - v'_{ij}) \mu_j . \quad (3.4.47)$$

In particular, by virtue of (3.4.22), for ideal gases we have

$$\mathcal{A}_i = \sum_j (v_{ij} - v'_{ij}) \zeta_j + RT \sum_j (v_{ij} - v'_{ij}) \ln(C_j/V) . \quad (3.4.48)$$

From (3.4.45, 47) we easily obtain the appropriate equation for the Gibbs potential $G = F + pV$. It is of the form

$$dG(T, p, \xi) = -S dT + V dp + \sum_i \mathcal{A}_i d\xi_i . \quad (3.4.49)$$

As it follows from the third formulation of the second law of thermodynamics (Sect. 2.2.3), for isothermal and isochoric processes (when $dT = 0, dV = 0$) the stability condition is the minimum of free energy $F(V, \xi)$, i.e.

$$\partial F(T, V, \xi) / \partial \xi_i = 0, \quad i = 1, \dots, s , \quad (3.4.50)$$

$$\partial^2 F(T, V, \xi) / \partial \xi_i \partial \xi_j = \text{positive definite} . \quad (3.4.51)$$

Equation (3.4.51) means that the matrix $(\partial^2 F / \partial \xi_i \partial \xi_k)_{T,V}$ is positive definite. Considering (3.4.46) we can write the conditions (3.4.50, 51) in terms of the affinity:

$$\mathcal{A}_i^0 = 0, \quad i = 1, \dots, s , \quad (3.4.52)$$

$$\partial \mathcal{A}_i(T, V, \xi) / \partial \xi_j = \text{positive definite} . \quad (3.4.53)$$

If the process is isothermal and isobaric, the stability condition is the minimum of the Gibbs potential $G(T, p, \xi)$. Considering (3.4.49), we see that in this case the stability conditions have the same form as (3.4.52, 53), but the isochoric derivative $(\partial \mathcal{A}_i / \partial \xi_k)_{T,V}$ must be now replaced by the isobaric one $(\partial \mathcal{A}_i / \partial \xi_k)_{T,p}$.

For an ideal gas, when (3.4.48) is valid, the necessary equilibrium condition (3.4.52) takes the form

$$\prod_{j=1}^r (C_j/V)^{v'_{ij} - v_{ij}} = \exp \left[-\alpha \sum_j (v'_{ij} - v_{ij}) \zeta_j \right], \quad i = 1, \dots, s , \quad (3.4.54)$$

which is equivalent to (3.4.7) {at $k_i/k_{-j} = \exp[\alpha \sum_j (v'_{ij} - v_{ij}) \zeta_j]$ } and, consequently, to (3.4.41).

If we compare (3.4.43) with (3.4.26), we readily find the reaction equations in terms of the extents of reaction:

$$\frac{d\xi_i}{dt} = V k_i \prod_{l=1}^r (C_l(\xi)/V)^{v'_{il}} - V k_{-i} \prod_{l=1}^r (C_l(\xi)/V)^{v_{il}}, \quad i = 1, \dots, s, \quad (3.4.55)$$

where $C_l(\xi)$ are defined by (3.4.44).

The jump $\xi_i \rightarrow \xi_i + N_A^{-1}$ with the frequency (3.4.27) occurs for the forward i th reaction, and the jump $\xi_i \rightarrow \xi_i - N_A^{-1}$ with the frequency (3.4.32) occurs for the backward i th reaction. Therefore, the following master equation is valid:

$$\begin{aligned} \frac{\partial w(\xi)}{\partial t} = N_A V \sum_i & \left\{ [\exp(-N_A^{-1} \partial/\partial \xi_i) - 1] \left[k_i \prod_l (C_l/V)^{v'_{il}} w(\xi) \right] \right. \\ & \left. + [\exp(N_A^{-1} \partial/\partial \xi_i) - 1] \left[k_{-i} \prod_l (C_l/V)^{v_{il}} w(\xi) \right] \right\}. \end{aligned} \quad (3.4.56)$$

Hence, the kinetic potential has the form

$$V(y, \xi) = RTV \sum_i f_i(\xi) \left\{ (e^{\alpha y_i} - 1) + (e^{-\alpha y_i} - 1) (k_{-i}/k_i) \prod_l \left[\frac{C_l(\xi)}{V} \right]^{v_{il} - v'_{il}} \right\}, \quad (3.4.57)$$

where

$$f_i(\xi) = k_i \prod_l [C_l(\xi)/V]^{v'_{il}}, \quad \alpha = (RT)^{-1}. \quad (3.4.58)$$

Using (3.4.48), we easily find the image $R(y, \mathcal{A}) = V(y, \xi(\mathcal{A}))$. Namely, we have

$$R(y, \mathcal{A}) = RTV \sum_{i=1}^s f_i[\xi(\mathcal{A})] [(e^{\alpha y_i} - 1) + (k_{-i}/k_i) (e^{-\alpha y_i} - 1) e^{\alpha \mathcal{A}_i}]. \quad (3.4.59)$$

It is easy to verify that (3.4.41) is a necessary and sufficient condition for the validity of the generating equation (3.2.50), i.e. for the equality $R(Y + \mathcal{A}, \mathcal{A}) = R(-y, \mathcal{A})$.

3.4.5 Chemical Reactions as Spatial or Continuum Fluctuational Processes

Let us consider the continuum versions of (3.4.34–37). We will be interested in fluctuations not only in time, but also in space. We will take the random molar concentration $c_j(\mathbf{r})$ as the external thermodynamic parameter B_α . The pair (j, \mathbf{r}) plays the role of the subscript α ; here \mathbf{r} is the radius vector. The forces conjugate to $c_j(\mathbf{r})$ will be denoted by $x_j(\mathbf{r}) = \mu_j(\mathbf{r}) - \mu_j^0(\mathbf{r})$. They are now functions of \mathbf{r} .

In the continuum case the functionals $V[y(\mathbf{r}), c(\mathbf{r})]$ and $R[y(\mathbf{r}), x(\mathbf{r})]$ must be taken as the kinetic potential (3.4.35) and as the image (3.4.37), respectively. Furthermore, the probability density $w[c(\mathbf{r})]$ is also a functional, and the master equation now has the form of an equation with variational derivatives

$$\frac{\partial w[c(\mathbf{r}), t]}{\partial t} = \beta N_{\delta, c} V \left[-kT \frac{\delta}{\delta c(\mathbf{r})}, c(\mathbf{r}) \right] w[c(\mathbf{r}), t]. \quad (3.4.60)$$

To find the form of the functional $R[y(\mathbf{r}), x(\mathbf{r})]$, we divide the region V of the three-dimensional space into elementary subregions with volumes ΔV_k . We choose a point \mathbf{r}_k inside each subregion. Applying (3.4.37) to the k th subregion, we have

$$\begin{aligned} R_{\Delta V_k}(y(\mathbf{r}_k), x(\mathbf{r}_k)) &= \Delta V_k RT \sum_i k'_i \left\{ \left[\exp \left(\alpha \sum_j (v_{ij} - v'_{ij}) y_j(\mathbf{r}_k) \right) - 1 \right] \right. \\ &\quad \times \exp \left[\alpha \sum_l v'_{il} x_l(\mathbf{r}_k) \right] + \left[\exp \left(-\alpha \sum_j (v_{ij} - v'_{ij}) y_j(\mathbf{r}_k) \right) - 1 \right] \\ &\quad \left. \times \exp \left[\alpha \sum_l v_{il} x_l(\mathbf{r}_k) \right] \right\}. \end{aligned} \quad (3.4.61)$$

Here (3.4.41) is used. If we sum (3.4.61) over k , i.e. over the various subregions, and pass to the limit $\max_k \Delta V_k \rightarrow 0$, we obtain the complete functional in the form of an integral:

$$\begin{aligned} R[y(\mathbf{r}), x(\mathbf{r})] &= RT \sum_i k'_i \int \left\{ \left[\exp \left(\alpha \sum_j (v_{ij} - v'_{ij}) y_j(\mathbf{r}) \right) - 1 \right] \right. \\ &\quad \times \exp \left[\alpha \sum_l v'_{il} x_l(\mathbf{r}) \right] + \left[\exp \left(-\alpha \sum_j (v_{ij} - v'_{ij}) y_j(\mathbf{r}) \right) - 1 \right] \\ &\quad \left. \times \exp \left[\alpha \sum_l v_{il} x_l(\mathbf{r}) \right] \right\} d\mathbf{r}. \end{aligned} \quad (3.4.62)$$

This functional satisfies the generating equation (3.2.50).

3.4.6 Diffusion of a Gaseous Admixture in a Homogeneous Gas

Our goal now is to take into account the diffusion of reagents. In order to do this more conveniently, we have written in Sect. 3.4.5 the continuum master equation in terms of molar concentrations, but not in terms of extents of reaction.

First of all we consider the diffusion of one gaseous admixture in a homogeneous gas. Its molar concentration satisfies the ordinary diffusion equation

$$\partial c(\mathbf{r})/\partial t = D \Delta c(\mathbf{r}), \quad (3.4.63)$$

where

$$\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$$

and D is the diffusion constant. Equation (3.4.63) is linear. If we assume the one-time functional stationary probability density to be of the Gaussian type, we can apply the theory of a system with linear relaxation (described in Sect. 3.1.3) to the present example. In our case $c(\mathbf{r}) - c_0$ plays the role of A_α , where c_0 is the equilibrium molar concentration, and the subscript α has the meaning of a radius

vector \mathbf{r} . Hence, (3.1.18, 19) must be rewritten as

$$\dot{c}(\mathbf{r}) = - \int d(\mathbf{r}, \mathbf{r}') [c(\mathbf{r}') - c_0] d\mathbf{r}' , \quad (3.4.64)$$

$$F[c(\mathbf{r})] = \frac{1}{2} \int u(\mathbf{r}, \mathbf{r}') [c(\mathbf{r}) - c_0] [c(\mathbf{r}') - c_0] d\mathbf{r} d\mathbf{r}' . \quad (3.4.65)$$

In so doing, (3.1.28) and (3.3.3) take the form

$$V[y(\mathbf{r}), c(\mathbf{r}) - c_0] = \int y(\mathbf{r}) d(\mathbf{r}, \mathbf{r}') \left[\int u^{-1}(\mathbf{r}', \mathbf{r}'') y(\mathbf{r}'') d\mathbf{r}'' - c(\mathbf{r}') + c_0 \right] d\mathbf{r} d\mathbf{r}' , \quad (3.4.66a)$$

$$R[y(\mathbf{r}), x(\mathbf{r})] = \int y(\mathbf{r}) d(\mathbf{r}, \mathbf{r}') u^{-1}(\mathbf{r}', \mathbf{r}'') [y(\mathbf{r}'') - x(\mathbf{r}'')] d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' . \quad (3.4.66b)$$

Comparing (3.4.64) with (3.4.63), we see that the operator with matrix elements $d(\mathbf{r}, \mathbf{r}')$ coincides with the operator $-D\Delta$. Therefore, (3.4.66b) can be rewritten as

$$R[y(\mathbf{r}), x(\mathbf{r})] = -D \int y(\mathbf{r}) \Delta \left\{ \int u^{-1}(\mathbf{r}, \mathbf{r}') [y(\mathbf{r}') - x(\mathbf{r}')] d\mathbf{r}' \right\} d\mathbf{r} . \quad (3.4.67)$$

After using the vector formula

$$\int \varphi \Delta \psi dV = - \int \text{grad } \varphi \cdot \text{grad } \psi dV , \quad (3.4.68)$$

where the integral over the surface is omitted, we have

$$R[y(\mathbf{r}), x(\mathbf{r})] = D \int [\nabla y(\mathbf{r})] \cdot \nabla_r \{u^{-1}(\mathbf{r}, \mathbf{r}') [y(\mathbf{r}') - x(\mathbf{r}')] \} d\mathbf{r} d\mathbf{r}' . \quad (3.4.69)$$

Now we determine the matrix $u(\mathbf{r}, \mathbf{r}')$ appearing in (3.4.65). We first fix a certain small gas volume ΔV . We can regard $C = c \Delta V$ as the internal parameter A_1 . Formula (3.1.38) now takes the form $\partial F(C)/\partial C = x$. Hence, using (3.4.25) gives

$$\partial F(C)/\partial C = RT \ln(C/C_0) . \quad (3.4.70)$$

The expansion of this expression into a power series in terms of the deviation $C - C_0$ can be easily found:

$$\partial F(C)/\partial C = RT(C - C_0)/C_0 - \frac{1}{2} RT[(C - C_0)/C_0]^2 + \dots . \quad (3.4.71)$$

Integrating with respect to C and switching over to the concentrations $c = C/\Delta V$ gives

$$F(C) = RT \Delta V \left[\frac{1}{2} c_0^{-1} (c - c_0)^2 - \frac{1}{6} c_0^{-2} (c - c_0)^3 + \dots \right] + \text{const} . \quad (3.4.72)$$

Let us apply this formula to the diffusing gas under study. Dividing the total volume V into the elementary subvolumes ΔV_k and applying (3.4.72) to the k th subvolume, we have

$$F_{\Delta V_k}(c \Delta V_k) = RT[(c - c_0)^2/(2c_0) - (c - c_0)^3/(6c_0^2) + \dots] \Delta V_k + \text{const} . \quad (3.4.73)$$

Summing up the free energies of the various subvolumes and passing to the limit $\max_k \Delta V_k \rightarrow 0$, we obtain the free energy of the gas as a functional of $c(\mathbf{r})$:

$$F[c(\mathbf{r})] = RT \int \left[\frac{(c(\mathbf{r}) - c_0)^2}{2c_0} - \frac{(c(\mathbf{r}) - c_0)^3}{6c_0^2} + \dots \right] d\mathbf{r} + \text{const.} \quad (3.4.74)$$

Comparing the quadratic part of the integral (3.4.74) with (3.4.65), we obtain

$$u(\mathbf{r}, \mathbf{r}') = RT c_0^{-1} \delta(\mathbf{r} - \mathbf{r}'). \quad (3.4.75)$$

Consequently, $u^{-1}(\mathbf{r}, \mathbf{r}') = (c_0/RT) \delta(\mathbf{r} - \mathbf{r}')$, and from (3.4.69) we find

$$R[y(\mathbf{r}), x(\mathbf{r})] = \frac{Dc_0}{RT} \int [\nabla y(\mathbf{r})] \cdot \nabla [y(\mathbf{r}) - x(\mathbf{r})] d\mathbf{r}. \quad (3.4.76)$$

The spatial density corresponding to this image is

$$r_0(\nabla y, \nabla x) = \frac{Dc_0}{RT} (\nabla y) \cdot \nabla (y - x). \quad (3.4.77)$$

It is easy to verify that both the image and its density satisfy the generating equation

$$R[y(\mathbf{r}) + x(\mathbf{r}), x(\mathbf{r})] = R[-y(\mathbf{r}), x(\mathbf{r})]. \quad (3.4.78)$$

The image (3.4.76) is, of course, only an approximation to the exact one. The difference between the exact image and (3.4.76) is due to the fact that the actual exact functional $F[c(\mathbf{r})]$ of the free energy is nonquadratic.

To find the precise kinetic potential or its image, one can again divide the volume V into small subvolumes and replace the diffusion by jumps of molecules between the subvolumes. Then one can treat these jumps as first-order reactions, apply the theory of Sect. 3.4.3 and take the limit $\max_k \Delta V_k \rightarrow 0$. One can also consider the complicated diffusion model defined by

$$\hat{c}(\mathbf{r}) = \gamma \int p(\mathbf{r} - \mathbf{r}') c(\mathbf{r}') d\mathbf{r}' - \gamma c(\mathbf{r}). \quad (3.4.79)$$

Here γ is the mean frequency of the jumps $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{s}$, and $p(\mathbf{s})$ is the probability density of the shift vector \mathbf{s} at the moment of jump. Considerations similar to those which were used for deriving (3.4.35, 37) lead to the following image for the above model:

$$\begin{aligned} R[y(\mathbf{r}), x(\mathbf{r})] &= RT \exp[\alpha(\mu^0 - \zeta)] \int d\mathbf{r} d\mathbf{r}' \gamma p(\mathbf{r} - \mathbf{r}') \{ \exp[\alpha(y(\mathbf{r}) - y(\mathbf{r}'))] - 1 \} \\ &\quad \times \exp[\alpha x(\mathbf{r}')]. \end{aligned} \quad (3.4.80)$$

Here we can write $p(\mathbf{r} - \mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')$ instead of $p(\mathbf{r} - \mathbf{r}')$ and by virtue of (3.4.23)

we can substitute c_0 for $\exp[\alpha(\mu^0 - \zeta)]$. If we now vary γ and $p(s)$ so that

$$\gamma[p(\mathbf{r} - \mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')] \rightarrow D\Delta_r \delta(\mathbf{r} - \mathbf{r}'), \quad (3.4.81)$$

we obtain from (3.4.80)

$$\begin{aligned} R[y(\mathbf{r}), x(\mathbf{r})] &= RTDc_0 \left\{ \int d\mathbf{r} \exp([\alpha y(\mathbf{r})]) [\nabla^2 \exp(\alpha x(\mathbf{r}) - \alpha y(\mathbf{r}))] \right. \\ &\quad \left. - \int d\mathbf{r} \nabla^2 \exp[\alpha x(\mathbf{r})] \right\}. \end{aligned} \quad (3.4.82)$$

The second integral in the braces can be reduced to an integral over the remote surface and may be omitted. The first integral in braces can be transformed as

$$\int d\mathbf{r} \exp(\alpha y) \nabla^2 \exp[\alpha(x - y)] = - \int d\mathbf{r} [\nabla \exp(\alpha y)] \cdot \nabla \exp[\alpha(x - y)]. \quad (3.4.83)$$

Hence, (3.4.82) takes the form

$$R[y(\mathbf{r}), x(\mathbf{r})] = \frac{Dc_0}{RT} \int \exp[\alpha x(\mathbf{r})] [\nabla y(\mathbf{r})] \cdot \nabla [y(\mathbf{r}) - x(\mathbf{r})] d\mathbf{r}. \quad (3.4.84)$$

This is the precise formula for the image of the kinetic potential in the case of linear diffusion in the ideal gas model. Like (3.4.76) it satisfies the generating equation (3.4.78). The kinetic potential

$$V[y(\mathbf{r}), c(\mathbf{r})] = \frac{D}{RT} \int [\nabla y(\mathbf{r})] [c(\mathbf{r}) \nabla y(\mathbf{r}) - RT \nabla c(\mathbf{r})] d\mathbf{r}. \quad (3.4.85)$$

corresponds to (3.4.84).

The master equation corresponding to this potential is the functional Fokker–Planck equation.

3.4.7 Chemical Reactions with Diffusion

Let the concentrations of various substances $c_j(\mathbf{r})$ satisfy the equations with diffusion:

$$\partial c_j(\mathbf{r})/\partial t = D_j \Delta c_j(\mathbf{r}) + \Xi_j, \quad j = 1, \dots, r, \quad (3.4.86)$$

where Ξ_j denotes the right-hand side of (3.4.5), which describes the chemical reactions. Writing down the image of the type (3.4.84) for each reagent, summing over j and adding the functional (3.4.62), we obtain the total image of the kinetic potential

$$R[y(\mathbf{r}), x(\mathbf{r})] = \int r_0(y(\mathbf{r}), x(\mathbf{r}), \nabla y(\mathbf{r}), \nabla x(\mathbf{r})) d\mathbf{r}, \quad (3.4.87)$$

where

$$\begin{aligned}
 r_0(y(\mathbf{r}), x(\mathbf{r}), \nabla y(\mathbf{r}), \nabla x(\mathbf{r})) \\
 = \sum_j \alpha D_j c_j^0 \exp(\alpha x_j(\mathbf{r})) [\nabla y_j(\mathbf{r})] \cdot \nabla [y_j(\mathbf{r}) - x_j(\mathbf{r})] \\
 + RT \sum_i k'_i \left\{ \left[\exp \left(\alpha \sum_j (v_{ij} - v'_{ij}) y_j(\mathbf{r}) \right) - 1 \right] \exp \left(\alpha \sum_j v'_{ij} x_j(\mathbf{r}) \right) \right. \\
 \left. + \left[\exp \left(-\alpha \sum_j (v_{ij} - v'_{ij}) y_j(\mathbf{r}) \right) - 1 \right] \exp \left(\alpha \sum_j v_{ij} x_j(\mathbf{r}) \right) \right\}. \quad (3.4.88)
 \end{aligned}$$

Of course, it satisfies the generating equation.

In conclusion we note that one can also take into account the thermal effect of reactions and the heat conduction accompanying chemical reactions. This leads to an increase in the number of parameters considered and makes the form of the kinetic potential and its image more complex.

In this section we have treated chemical reactions in the ideal gas model, which is suitable for sufficiently rarefied gases or solutions. If this condition is not fulfilled, one can turn to another model which is more realistic. In this case the kinetic potential and its image have other forms, but they must satisfy the generating equation as before.

3.5 Generating Equation for the Kinetic Potential Spectrum

3.5.1 The Kinetic Potential Spectrum

In Sect. 2.4 it was shown that for an arbitrary Markov Process $y(t)$ the condition of nonnegativity of the various probability densities leads to the fact that the function $\Phi(v, y)$ in the master equation (2.3.23) can be represented in the form (2.4.33), $g(z, y)$ being nonnegative. We will use this fact, taking $B_\alpha(t)$ as $y(t)$. The function $\Phi(v, y)$ is related to the kinetic potential by (3.1.10), i.e. by

$$V(y, B) = kT\Phi(\beta y, B). \quad (3.5.1)$$

We insert (2.4.33) (where y'' is replaced by B) into this and obtain

$$V(y, B) = K_\alpha(B) y_\alpha + kT \int_{-\infty}^{\infty} [\exp(\beta y z) - 1 - \beta y z] z^{-2} g(z, B) dz. \quad (3.5.2)$$

Strictly speaking, here $v = iu$ is pure imaginary, but by analytic continuation the last equation can be extended also to other values of the argument v . Denoting $\beta z = s$, from (3.5.2) we obtain

$$V(y, B) = K_\alpha(B) y_\alpha + \int_{-\infty}^{\infty} [\exp(ys) - 1 - ys] s^{-2} g(kTs, B) ds. \quad (3.5.3)$$

If we substitute (3.5.3) into the formula (3.1.32) defining the image, we obtain

$$R(y, x) = \kappa_\alpha(x) y_\alpha + \int_{-\infty}^{\infty} [\exp(ys) - 1 - ys] s^{-2} G(s, x) ds , \quad (3.5.4)$$

where

$$G(s, x) = \int g(kTs, B) w_x(B) dB \quad (3.5.5)$$

and $\kappa_\alpha(x)$ is defined by (3.1.42).

The function $G(s, x)$ is called the kinetic potential spectrum. From the conditions (2.4.34) it follows that the spectrum satisfies analogous conditions:

$$G(s, x) \geq 0, \quad \int_{-\infty}^{\infty} g(s, x) ds < \infty . \quad (3.5.6)$$

The spectrum has a macroscopic nature like the kinetic potential and its image, i.e. it does not contain the Boltzmann constant (which is a small parameter) except in a product with some great parameter.

3.5.2 The Generating Equation

Substituting (3.5.4) into the generating equation (3.2.50) gives

$$\begin{aligned} \kappa_\alpha(x) (y_\alpha + x_\alpha) + \int_{-\infty}^{\infty} [\exp(ys + xs) - 1 - ys - xs] s^{-2} G(s, x) ds \\ = -\varepsilon_\alpha \kappa_\alpha(\varepsilon x) y_\alpha + \int_{-\infty}^{\infty} [\exp(-\varepsilon ys) - 1 + \varepsilon ys] s^{-2} G(s, \varepsilon x) ds . \end{aligned} \quad (3.5.7)$$

Putting $y = 0$, we have

$$\kappa_\alpha(x) x_\alpha + \int_{-\infty}^{\infty} [\exp(xs) - 1 - xs] s^{-2} G(s, x) ds = 0 . \quad (3.5.8)$$

Equation (3.5.8) is nothing but (3.1.36) applied to the canonical representation (3.5.4). We now differentiate (3.5.7) with respect to y_α and then set $y = 0$. This leads to

$$\kappa_\alpha(x) + \varepsilon_\alpha \kappa_\alpha(\varepsilon x) = - \int_{-\infty}^{\infty} [\exp(xs) - 1] s_\alpha s^{-2} G(s, x) ds . \quad (3.5.9)$$

When all the parameters B_α are time-even (i.e. all $\varepsilon_\alpha = 1$), this equation takes the form

$$\kappa_\alpha(x) = -\frac{1}{2} \int [\exp(xs) - 1] s_\alpha s^{-2} G(s, x) ds . \quad (3.5.10)$$

Consequently, in this case the spectrum $G(s, x)$ determines the whole vector $\kappa_\alpha(x)$. In the general case the spectrum determines only the time-even part of $\kappa_\alpha(x)$:

$$\kappa_\alpha^+(x) = \frac{1}{2} [\kappa_\alpha(x) + \varepsilon_\alpha \kappa_\alpha(\varepsilon x)] , \quad (3.5.11)$$

which remains unchanged under time reversal. The odd part

$$\kappa_\alpha^-(x) = \frac{1}{2} [\kappa_\alpha(x) - \varepsilon_\alpha \kappa_\alpha(\varepsilon x)] , \quad (3.5.12)$$

which changes sign under time reversal, must be preassigned additionally. From (3.9, 11, 12) we have

$$\begin{aligned} \kappa_\alpha(x) &= \kappa_\alpha^+(x) + \kappa_\alpha^-(x) \\ &= \kappa_\alpha^-(x) - \frac{1}{2} \int_{-\infty}^{\infty} [\exp(xs) - 1] s_\alpha s^{-2} G(s, x) ds . \end{aligned} \quad (3.5.13)$$

Substituting (3.5.13) into (3.5.8) gives

$$\kappa_\alpha^-(x) x_\alpha = - \int_{-\infty}^{\infty} \{[\exp(xs)] (1 - xs/2) - 1 - xs/2\} s^{-2} G(s, x) ds . \quad (3.5.14)$$

This equation is the only restriction imposed on the time-odd part $\kappa_\alpha^-(x)$ of $\kappa_\alpha(x)$. In the case of time-even parameters we have $\kappa_\alpha^-(x) = 0$, so that the right-hand side of (3.5.14) must be equal to zero.

In (3.5.7) we now consider the terms of quadratic and higher orders in y . Extracting the terms linear in y and also those independent of y from (3.5.7), we obtain

$$\begin{aligned} &\int \exp(xs) [\exp(izs) - 1 - izs] s^{-2} G(s, x) ds \\ &= \int_{-\infty}^{\infty} [\exp(izs') - 1 - izs'] (s')^{-2} G(-\varepsilon s', \varepsilon x) ds' , \end{aligned} \quad (3.5.15)$$

where we have put iz instead of y , and $-\varepsilon s$ has been denoted by s' .

Carrying out the inverse Fourier transformation of (3.5.15) with respect to z , we obtain

$$\exp(xs) G(s, x) = G(-\varepsilon s, \varepsilon x) \quad \text{for } s \neq 0 . \quad (3.5.16)$$

Thus, the spectrum $G(s, x)$ satisfying the conditions (3.5.6, 16) determines the whole image $R(y, x)$ except the time-odd part $\kappa_\alpha^-(x)$ restricted by condition (3.5.14). According to (3.5.4) and (3.1.41), we have

$$\sum_{m=2}^{\infty} \frac{\beta^{m-1}}{m!} \kappa_{\alpha_1 \dots \alpha_m}(x) y_{\alpha_1} \dots y_{\alpha_m} = \int_{-\infty}^{\infty} [\exp(ys) - 1 - ys] s^{-2} G(s, x) ds . \quad (3.5.17)$$

From (3.5.17) we see that the diffusion coefficients $\kappa_{\alpha_1 \alpha_2}(x), \kappa_{\alpha_1 \alpha_2 \alpha_3}(x), \dots$, which describe the fluctuations, determine the spectrum and vice versa. Using (3.5.10), we find that in the case of time-even parameters these coefficients completely determine the nonfluctuational coefficient $\kappa_\alpha(x)$. In the general case we also have the above-mentioned freedom of choice of $\kappa_\alpha^-(x)$.

The inverse problem often arises, namely, the problem of determining the coefficient functions describing the fluctuations, i.e. the problem of determining the total image $R(y, x)$ by the first coefficient $\kappa_\alpha(x)$ defined by the phenomenological equations and by free energy. From the above theory it can be seen that in order to

solve the problem, we must choose the spectrum $G(y, a)$ satisfying the conditions (3.5.6), the generating equation (3.5.16) and additional equations (3.5.8, 9). In doing so, of course, the choice of the spectrum is ambiguous. However, physical considerations concerning the mechanism of the fluctuational process and reasons of simplicity can help to specify the spectrum. In the following, examples of a few possible choices are written explicitly.

3.5.3 Examples of Spectra

1. Let us take the image (3.3.37) for the diode model of nonlinear resistance. Comparing (3.3.37) with (3.5.4) gives

$$\kappa_1(U) = -I_1 [\exp(\beta e p U) - \exp(-\beta e q U)], \quad (3.5.18)$$

$$\begin{aligned} & \frac{I_1}{\beta e} \{ [\exp(-\beta e y) - 1 + \beta e y] \exp(\beta e p U) \\ & \quad + [\exp(\beta e y) - 1 - \beta e y] \exp(-\beta e q U) \} \\ & = \int [\exp(ys) - 1 - ys] s^{-2} G(s, U) ds. \end{aligned} \quad (3.5.19)$$

From (3.5.19) we easily obtain

$$G(s, U) = \beta e I_1 [\exp(\beta e p U) \delta(s + \beta e) + \exp(-\beta e q U) \delta(s - \beta e)]. \quad (3.5.20)$$

The ratio e/kT is regarded as a macroscopic quantity.

It is obvious that the conditions (3.5.6) are fulfilled for the spectrum (3.5.20). It is also easy to verify that the spectrum satisfies the generating equation (3.5.13). Furthermore, (3.5.10) is valid for (3.5.18, 20).

2. We now turn to chemical reactions, which are analysed by means of extents of reaction. For this case we have obtained the image (3.4.59). Comparing it with (3.5.4), we readily find

$$\begin{aligned} G(s_1, s_2, A_1, A_2) &= \alpha V f_1[\xi(A)] [\delta(s_1 - \alpha) + \exp(A_1 \alpha) \\ &\quad \times \delta(s_1 + \alpha)] \delta(s_2) + \alpha V f_2[\xi(A)] \\ &\quad \times [\delta(s_2 - \alpha) + \exp(A_2 \alpha) \delta(s_2 + \alpha)] \delta(s_1) \end{aligned} \quad (3.5.21)$$

for the case of two reactions. Both the terms on the right-hand side are analogous to (3.5.20) and satisfy an equation of the type (3.5.16) at $\varepsilon_\alpha = 1$. In the examples considered above the parameters are time-even. We now proceed to the case of parameters of different time-parity.

3. Let us take the image (3.3.3) corresponding to the case of linear relaxation and quadratic free energy. Comparing it with (3.5.4) gives

$$\kappa_\alpha(x) = l_{\alpha, \rho} x_\rho, \quad (3.5.22)$$

$$l_{\alpha, \rho} y_\alpha y_\rho = - \int_{-\infty}^{\infty} [\exp(ys) - 1 - ys] s^{-2} G(s, x) ds, \quad (3.5.23)$$

where

$$l_{\alpha,\rho} = -d_{\alpha\rho} u_{\gamma\rho}^{-1}. \quad (3.5.24)$$

Let us seek $G(s, x) = G(s)$ satisfying (3.5.23) in the form

$$G(s) = C\delta(s). \quad (3.5.25)$$

The constant C in (3.5.25) can be found from the equation

$$\sum_{\beta} l_{\beta,\beta} = -\frac{1}{2} \int_{-\infty}^{\infty} G(s) ds, \quad (3.5.26)$$

which is obtained from (3.5.23) by differentiating twice with respect to y_{β} , summing over β and equating y to zero. Substituting (3.5.25) into (3.5.26) yields

$$C = -2 \sum_{\beta} l_{\beta,\beta}. \quad (3.5.27)$$

If we now insert (3.5.25) into (3.5.23), we obtain

$$l_{\alpha,\gamma} y_{\alpha} y_{\gamma} = y_{\alpha} y_{\gamma} \sum_{\beta} l_{\beta,\beta} \int s_{\alpha} s_{\gamma} s^{-2} \delta(s) ds. \quad (3.5.28)$$

The integral on the right-hand side of (3.5.28) gives an indeterminate form of the type $0/0$. In order to remove this indeterminate form one should use the refined delta functions introduced in Appendix 2, Sect. A2.2. In doing so, (3.5.25) should be replaced by

$$G(s) = -2c_r \sum_{\beta} l_{\beta,\beta} p(s/s) \delta_{is}(s), \quad (3.5.29)$$

and (3.5.28) assumes the form

$$l_{\alpha,\gamma} y_{\alpha} y_{\gamma} = y_{\alpha} y_{\gamma} \sum_{\beta} l_{\beta,\beta} \int m_{\alpha} m_{\gamma} p(\mathbf{m}) d\Omega. \quad (3.5.30)$$

Here (A2.23) has been used, and the integral corresponds to integration with respect to the generalized polar angles of the r -dimensional space. From the theory of Sect. A2.2 it is seen that (3.5.30) will be satisfied if the probability density (A2.32) at

$$s_{\alpha\beta} = \frac{1}{2}(l_{\alpha,\beta} + l_{\beta,\alpha}) / \sum_{\beta} l_{\beta,\beta} \quad (3.5.31)$$

is taken as the probability density $p(\mathbf{m})$. We assume that in the case under study $\sum_{\beta} l_{\beta,\beta} \neq 0$.

The spectrum (3.5.29) is nonnegative. Let us apply (3.5.16) to this spectrum. Since (3.5.16) is invalid at $s = 0$, we should regard the delta function in (3.5.29) as an approximate one, having nonzero but very small width ϵ . Then the point $s = 0$ is unessential, and there is no need to take it into account. Substituting (3.5.29) into (3.5.16) gives

$$l_{\alpha,\beta} + l_{\beta,\alpha} = \epsilon_{\alpha} \epsilon_{\beta} (l_{\alpha,\beta} + l_{\beta,\alpha}). \quad (3.5.32)$$

In order to obtain the stronger equation

$$l_{\alpha,\beta} = \varepsilon_\alpha \varepsilon_\beta l_{\beta,\alpha}, \quad (3.5.33)$$

i.e. (3.3.5), one should use (3.5.22, 9).

In the above example the spectra are discrete. Of course, this is not always so. The spectrum is continuous if the Markov process is a complex process including jumps whose length is random and has the continuous probability density.

3.6 Notes on References to Chapter 3

Time symmetry of the Markov processes was first investigated by Kolmogorov [3.1]. Later it was considered by van Kampen [3.7]. In the case of time-even parameters the generating equation (in its other form, namely, the operational form) was first obtained by exploiting the time reversibility of the Markov process [Ref. 3.8, eq. (7)]. The master equation coefficient images, which can be used to write precise relations following from time reversibility, were introduced in the same work. For the case of time-even and time-odd parameters the generating equation (in operational form) was obtained in [3.9].

The diode model of nonlinear resistance was suggested in [3.10]. In this work the paradox related to thermal fluctuation detection, which supposedly contradicts the second law of thermodynamics, was also solved.

Readers can become acquainted with chemical reactions and the application of equilibrium and nonequilibrium thermodynamics to them in the books [3.11, 12]. However, in these books the kinetic potential and the validity of the generating equation for chemical reactions were not considered; thus, the present approach is original. The spectral representation of the kinetic potential (“canonic representation”) and the corresponding consequences of time reversibility were considered in [3.13].

4. Consequences of the Markov Generating Equation

In this chapter the various exact and approximate Markov fluctuation–dissipation relations (FDRs) are derived from the generating equation written for the kinetic potential image. The simplest of these FDRs, namely, one-subscript relation expresses the absence of the detection of thermal fluctuations in nonlinear systems. This is in accordance with the second law of thermodynamics.

Two-subscript or linear relations, in particular, the reciprocal Onsager–Casimir relation, were obtained by other methods in the 1930s and 1940s. FDRs with a larger number of subscripts refer to nonlinear nonequilibrium thermodynamics. They were obtained much later (in the 1960s).

Linear and nonlinear relations can be applied for determining the approximate Markov operator and therefore for calculating the statistical properties of internal parameter fluctuations in the Markov model. For many examples referring to mechanics, electricity and chemistry the validity of the reciprocal relations will be shown, the two-time correlator of internal parameters or the corresponding spectral density will be found, and the Markov operator built up in the nonlinear cases.

Furthermore, the more special generating equation, which is based only on the dynamic equilibrium principle, will be used to derive the inequality expressing the second law of thermodynamics. In other words, the *H*-theorem of Markov non-equilibrium thermodynamics will be proved.

4.1 Markov FDRs

4.1.1 Relations for Images of Coefficient Functions

According to (3.1.41), the kinetic potential image can be represented in the form of a series whose coefficients are the images $\kappa_{\alpha_1 \dots \alpha_m}(x)$ of the coefficient functions $K_{\alpha_1 \dots \alpha_m}(B)$. Substituting (3.1.41) into (3.2.50) and using

$$R(y + x, x) = \sum_{l=1}^{\infty} \frac{1}{l!} \left(x, \frac{\partial}{\partial y} \right)^l R(y, x), \quad (4.1.1)$$

we obtain

$$\begin{aligned} & \sum_{m=1}^{\infty} \frac{1}{m!} (-1)^m \beta^m \kappa_{\alpha_1 \dots \alpha_m}(ex) \varepsilon_{\alpha_1} y_{\alpha_1} \dots \varepsilon_{\alpha_m} y_{\alpha_m} \\ & = \sum_{l=0}^{\infty} \frac{1}{l!} \beta^l x_{\gamma_1} \dots x_{\gamma_l} \sum_{k=1}^{\infty} \frac{1}{(k-l)!} \beta^{k-l} \kappa_{\alpha_1 \dots \alpha_{k-l} \gamma_1 \dots \gamma_l}(x) y_{\alpha_1} \dots y_{\alpha_{k-l}}. \end{aligned} \quad (4.1.2)$$

Separating the terms of the order of y^m from (4.1.2), we find

$$\begin{aligned} & \kappa_{\alpha_1 \dots \alpha_m}(x) - (-1)^m \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \kappa_{\alpha_1 \dots \alpha_m}(ex) \\ & = - \sum_{l=1}^{\infty} \frac{1}{l!} \beta^l \kappa_{\alpha_1 \dots \alpha_m \gamma_1 \dots \gamma_l}(x) x_{\gamma_1} \dots x_{\gamma_l}. \end{aligned} \quad (4.1.3)$$

Here m runs through the values $0, 1, 2, \dots$, and $\kappa_{\alpha_1 \dots \alpha_m} = 0$ at $m = 0$.

In particular, setting $m = 0$ and $m = 1$, we obtain from (4.1.3)

$$0 = -\beta \kappa_{\gamma}(x) x_{\gamma} - \frac{1}{2} \beta^2 \kappa_{\gamma\delta}(x) x_{\gamma} x_{\delta} - \frac{1}{6} \beta^3 \kappa_{\gamma\delta\rho}(x) x_{\gamma} x_{\delta} x_{\rho} - \frac{1}{24} \beta^4 \kappa_{\gamma\delta\rho\sigma}(x) x_{\gamma} x_{\delta} x_{\rho} x_{\sigma} - \dots, \quad (4.1.4)$$

$$\kappa_{\alpha}(x) + \varepsilon_{\alpha} \kappa_{\alpha}(ex) = -\beta \kappa_{\alpha\gamma}(x) x_{\gamma} - \frac{1}{2} \beta^2 \kappa_{\alpha\gamma\delta}(x) x_{\gamma} x_{\delta} - \frac{1}{6} \kappa_{\alpha\gamma\delta\rho} x_{\gamma} x_{\delta} x_{\rho} - \dots. \quad (4.1.5)$$

Equation (4.1.4) is equivalent to (3.1.36) and can be derived from the dynamical equilibrium condition alone without using the time reversibility condition. Equations (4.1.5, 3) are based on time reversibility as well.

Let us introduce the notation

$$l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} = \frac{\partial^n \kappa_{\alpha_1 \dots \alpha_m}(x)}{\partial x_{\beta_1} \dots \partial x_{\beta_n}} \quad \text{for } x = 0, n = 0, 1, 2, \dots. \quad (4.1.6)$$

If we set $x = 0$ in (4.1.3), we have

$$\varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} l_{\alpha_1 \dots \alpha_m} = (-1)^m l_{\alpha_1 \dots \alpha_m} \quad (4.1.7)$$

or

$$l_{\alpha_1 \dots \alpha_m} = 0 \quad \text{for } \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} = -(-1)^m. \quad (4.1.8)$$

Differentiating (4.1.3) with respect to x and putting $x = 0$, we obtain

$$[1 - (-1)^m \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \varepsilon_{\beta}] l_{\alpha_1 \dots \alpha_m, \beta} = -(kT)^{-1} l_{\alpha_1 \dots \alpha_m \beta} \quad (m = 0, 1, \dots). \quad (4.1.9)$$

Further, one can differentiate (4.1.3) with respect to x_{β_1} and x_{β_2} and set $x = 0$, etc. This gives the set of equations connecting the quantities $l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n}$ for various m and n . Here we study only the relations concerning matrices $l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n}$ with four subscripts or fewer ($m + n \leq 4$).

4.1.2 Basic Fluctuation–Dissipation Relations

a) *The one-subscript relations.* Setting $m = 0$ in (4.1.9), we obtain

$$l_\beta = 0 \quad (4.1.10)$$

for any β . This equation or, in other words, the equation $\kappa_\beta(0) = 0$ is in agreement with the second law of thermodynamics. According to it, the fluxes $J_\alpha = \dot{A}_\alpha$ are equal to zero in the absence of external forces, i.e. at the thermodynamic equilibrium. This was discussed in Sect. 3.3.3 for the example of a nonlinear resistor.

b) *The two-subscript relations.* Putting $m = 1$ in (4.1.9), we find

$$l_{\alpha\beta} = -kT(1 + \varepsilon_\alpha \varepsilon_\beta)l_{\alpha,\beta}. \quad (4.1.11)$$

Further, if we differentiate (4.1.4) with respect to x_α and x_β and then set $x = 0$, we get

$$l_{\alpha\beta} = -kT(l_{\alpha,\beta} + l_{\beta,\alpha}). \quad (4.1.12)$$

There are no other independent two-subscript relations. Subtracting (4.1.11) from (4.1.12) gives

$$l_{\beta,\alpha} = \varepsilon_\alpha \varepsilon_\beta l_{\alpha,\beta}. \quad (4.1.13)$$

Equations (4.1.12, 13) can be regarded as the basic two-subscript FDRs. Relation (4.1.13) is called the Onsager–Casimir relation. In Markov nonequilibrium thermodynamics, (4.1.13) is the only relation [if (4.1.10) is not considered] that does not contain the diffusion matrices $l_{\alpha_1 \dots \alpha_m}(0)$ ($m \geq 2$) and their derivatives. In the case of time-even parameters relation (4.1.13) assumes the form

$$l_{\beta,\alpha} = l_{\alpha,\beta}. \quad (4.1.14)$$

This equation was obtained by Onsager in 1931 and is named after him.

c) *The three-subscript relations.* Let us differentiate (4.1.4) with respect to x_α , x_β , x_γ and (4.1.5) with respect to x_β , x_γ and put $x = 0$. We find

$$l_{\alpha\beta\gamma} + kT(l_{\alpha\beta,\gamma} + l_{\alpha\gamma,\beta} + l_{\beta\gamma,\alpha}) + (kT)^2(l_{\alpha,\beta\gamma} + l_{\beta,\alpha\gamma} + l_{\gamma,\alpha\beta}) = 0, \quad (4.1.15a)$$

$$l_{\alpha\beta\gamma} + kT(l_{\alpha\beta,\gamma} + l_{\alpha\gamma,\beta}) + (kT)^2(1 + \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma)l_{\alpha,\beta\gamma} = 0. \quad (4.1.15b)$$

Subtracting (4.1.15b) from (4.1.15a) yields

$$l_{\beta\gamma,\alpha} = kT(\varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma l_{\alpha,\beta\gamma} - l_{\beta,\alpha\gamma} - l_{\gamma,\alpha\beta}). \quad (4.1.16)$$

We now use (4.1.9) for $m = 2$. We have

$$l_{\alpha\beta\gamma} = -kT(1 - \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma)l_{\alpha\beta,\gamma}. \quad (4.1.17)$$

If we substitute (4.1.16) into (4.1.17), we obtain

$$l_{\alpha\beta\gamma} = (kT)^2(1 - \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma)(l_{\alpha,\beta\gamma} + l_{\beta,\alpha\gamma} + l_{\gamma,\alpha\beta}). \quad (4.1.18)$$

Equations (4.1.16, 18) are the basic relations. There are no other independent three-subscript relations. Thus, setting $m = 3$ in (4.1.8) gives the relation $l_{\alpha\beta\gamma} = 0$ at $\varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma = 1$, which follows from (4.1.18).

According to (4.1.16, 18), all three-subscript diffusion matrices $l_{\alpha\beta,\gamma}$, $l_{\alpha\beta\gamma}$ are expressed by a nondiffusion matrix $l_{\alpha,\beta\gamma}$, which can be found by using the phenomenological equation and free energy. In this respect the three-subscript case is analogous to the two-subscript case in which the diffusion matrix $l_{\alpha\beta}$ is expressed by the nondiffusion matrix $l_{\alpha,\beta}$ according to (4.1.12).

d) The four-subscript relations. Differentiating (4.1.4) with respect to x_α , x_β , x_γ , x_δ at the zero point, we find

$$\begin{aligned} l_{\alpha\beta\gamma\delta} + kT(l_{\alpha\beta\gamma,\delta} + l_{\alpha\beta\delta,\gamma} + l_{\alpha\gamma\delta,\beta} + l_{\beta\gamma\delta,\alpha}) + (kT)^2(l_{\alpha\beta,\gamma\delta} + l_{\alpha\gamma,\beta\delta} + l_{\alpha\delta,\beta\gamma} + l_{\beta\gamma,\alpha\delta} \\ + l_{\beta\delta,\alpha\gamma} + l_{\gamma\delta,\alpha\beta}) + (kT)^3(l_{\alpha,\beta\gamma\delta} + l_{\beta,\alpha\gamma\delta} + l_{\gamma,\alpha\beta\delta} + l_{\delta,\alpha\beta\gamma}) = 0. \end{aligned} \quad (4.1.19)$$

If we differentiate (4.1.5) with respect to x_β , x_γ , x_δ at the zero point, we obtain

$$\begin{aligned} l_{\alpha\beta\gamma\delta} + kT(l_{\alpha\beta\gamma,\delta} + l_{\alpha\beta\delta,\gamma} + l_{\alpha\gamma\delta,\beta}) + (kT)^2(l_{\alpha\beta,\gamma\delta} + l_{\alpha\gamma,\beta\delta} + l_{\alpha\delta,\beta\gamma}) \\ + (1 + \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta)l_{\alpha,\beta\gamma\delta} = 0. \end{aligned} \quad (4.1.20)$$

Finally, if we take (4.1.3) at $m = 2$, $\alpha_1 = \alpha$, $\alpha_2 = \beta$, differentiate it with respect to x_γ and x_δ , and set $x = 0$, we have

$$l_{\alpha\beta\gamma\delta} + kT(l_{\alpha\beta\gamma,\delta} + l_{\alpha\beta\delta,\gamma}) + (kT)^2(1 - \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta)l_{\alpha\beta,\gamma\delta} = 0. \quad (4.1.21)$$

Subtracting (4.1.20) from (4.1.19) gives

$$\begin{aligned} l_{\beta\gamma\delta,\alpha} + kT(l_{\beta\gamma,\alpha\delta} + l_{\beta\delta,\alpha\gamma} + l_{\gamma\delta,\alpha\beta}) \\ + (kT)^2(l_{\beta,\alpha\gamma\delta} + l_{\gamma,\alpha\beta\delta} + l_{\delta,\alpha\beta\gamma} - \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta l_{\alpha,\beta\gamma\delta}) = 0. \end{aligned} \quad (4.1.22)$$

Further, subtracting (4.1.21) from (4.1.20), we find

$$l_{\alpha\gamma\delta,\beta} + kT(l_{\alpha\gamma,\beta\delta} + l_{\alpha\delta,\beta\gamma} + \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta l_{\alpha\beta,\gamma\delta}) + (kT)^2(1 + \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta)l_{\alpha,\beta\gamma\delta} = 0. \quad (4.1.23)$$

If we interchange α and β ($\alpha \rightleftharpoons \beta$), we have

$$l_{\beta\gamma\delta,\alpha} + kT(l_{\beta\gamma,\alpha\delta} + l_{\beta\delta,\alpha\gamma} + \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta l_{\alpha\beta,\gamma\delta}) + (kT)^2(1 + \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta)l_{\beta,\alpha\gamma\delta} = 0. \quad (4.1.24)$$

We now subtract (4.1.24) from (4.1.22) and obtain

$$l_{\gamma\delta,\alpha\beta} - \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta l_{\alpha\beta,\gamma\delta} + kT[l_{\gamma,\alpha\beta\delta} + l_{\delta,\alpha\beta\gamma} - \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta(l_{\alpha,\beta\gamma\delta} + l_{\beta,\alpha\gamma\delta})] = 0. \quad (4.1.25)$$

If we introduce the notation

$$c_{\alpha\beta,\gamma\delta} = (kT)^{-1}l_{\alpha\beta,\gamma\delta} + l_{\alpha,\beta\gamma\delta} + l_{\beta,\alpha\gamma\delta}, \quad (4.1.26)$$

equation (4.1.25) takes the form

$$c_{\gamma\delta,\alpha\beta} = \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta c_{\alpha\beta,\gamma\delta}. \quad (4.1.27)$$

If (4.1.26) is solved for $l_{\alpha\beta,\gamma\delta}$, and the result

$$l_{\alpha\beta,\gamma\delta} = kT(c_{\alpha\beta,\gamma\delta} - l_{\alpha,\beta\gamma\delta} - l_{\beta,\alpha\gamma\delta}) \quad (4.1.28)$$

is substituted into (4.1.22), we have

$$l_{\alpha\beta\gamma,\delta} = (kT)^2(l_{\alpha,\beta\gamma\delta} + l_{\beta,\alpha\gamma\delta} + l_{\gamma,\alpha\beta\delta} + \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta l_{\delta,\alpha\beta\gamma} - c_{\alpha\beta,\gamma\delta} - c_{\alpha\gamma,\beta\delta} - c_{\beta\gamma,\alpha\delta}). \quad (4.1.29)$$

Finally, using (4.1.29) and the formula

$$(1 + \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta)l_{\alpha\beta\gamma,\delta} = -(kT)^{-1}l_{\alpha\beta\gamma\delta} \quad (4.1.30)$$

following from (4.1.9) at $m = 3$, we arrive at

$$\begin{aligned} l_{\alpha\beta\gamma\delta} &= (kT)^3(1 + \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta) \\ &\times (c_{\alpha\beta,\gamma\delta} + c_{\alpha\gamma,\beta\delta} + c_{\beta\gamma,\alpha\delta} - l_{\alpha,\beta\gamma\delta} - l_{\beta,\alpha\gamma\delta} - l_{\gamma,\alpha\beta\delta} - l_{\delta,\alpha\beta\gamma}). \end{aligned} \quad (4.1.31)$$

Equations (4.1.27–29, 31) are regarded as the basic four-subscript FDRs. It is easy to check that they exhaust all independent four-subscript relations.

We see that in the four-subscript case the nondiffusion matrix $l_{\alpha,\beta\gamma\delta}$ does not completely determine the diffusion matrices $l_{\alpha\beta,\gamma\delta}$, $l_{\alpha\beta\gamma,\delta}$, $l_{\alpha\beta\gamma\delta}$. For the complete determination of the latter it is necessary to specify the matrix $c_{\alpha\beta,\gamma\delta}$, which is called the dissipationally undeterminable matrix and must satisfy the condition (4.1.27). In this respect the four-subscript case is essentially different from the two- and three-subscript cases.

The number of independent elements (parameters) of the matrix $c_{\alpha\beta,\gamma\delta}$ decreases due to the symmetry conditions $c_{\alpha\beta,\gamma\delta} = c_{\beta\alpha,\gamma\delta} = c_{\alpha\beta,\delta\gamma}$ and the condition (4.1.27). An additional decrease of the number of dissipationally undeterminable parameters occurs when the system under study has certain symmetry properties, for example, rotation symmetry (isotropy).

4.1.3 Modified FDRs

Besides the version described in Sects. 4.1.1, 2 a modified version of the theory can be constructed. In this version the generating equation (3.2.54) and the expansion (3.1.54) are taken as the initial ones. Instead of (4.1.6) we now introduce the matrices

$$L_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} = \frac{\partial^n \lambda_{\alpha_1 \dots \alpha_m}(X)}{\partial X_{\beta_1} \dots \partial X_{\beta_n}} \quad \text{for } X = 0. \quad (4.1.32)$$

The functions $\lambda_{\alpha_1 \dots \alpha_m}(X)$ are defined by (3.1.55). It is easy to see that in this version one can carry out calculations analogous to those of Sects. 4.1.1, 2. As a result, one can obtain modified FDRs, which differ from those of Sects. 4.1.1, 2 only in containing k instead of kT . For example, we have

$$L_{\alpha\beta} = -k(L_{\alpha,\beta} + L_{\beta,\alpha}), \quad (4.1.33a)$$

$$L_{\beta,\alpha} = \varepsilon_\alpha\varepsilon_\beta L_{\alpha,\beta}, \quad (4.1.33b)$$

$$L_{\alpha\beta,\gamma} = k(\varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma L_{\gamma,\alpha\beta} - L_{\alpha,\beta\gamma} - L_{\beta,\alpha\gamma}), \quad (4.1.33c)$$

$$L_{\alpha\beta\gamma} = 2k^2 g_{\alpha\beta\gamma}^-(L_{\alpha,\beta\gamma} + L_{\beta,\alpha\gamma} + L_{\gamma,\alpha\beta}) \quad (2g_{\alpha\beta\gamma}^- = 1 - \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma) \quad (4.1.33d)$$

instead of (4.1.12, 13, 16, 18). These relations are exact, as are the FDRs of Sect. 4.1.2.

4.1.4 Generalization of FDRs to the Case of an External Magnetic Field or Other Time-Odd Parameters

The condition of time reversibility (3.2.1), which is fundamental for the theory, is not valid if the system under study is put in an external magnetic field or if the system rotates, etc.; in other words, if the Hamiltonian $\mathcal{H}(q, p)$ depends on time-odd external parameters. For a magnetic field we have the Hamiltonian $\mathcal{H}(q, p, \mathbf{H})$. Instead of (3.2.1) it now satisfies the equation

$$\mathcal{H}(q, -p, -\mathbf{H}) = \mathcal{H}(q, p, \mathbf{H}). \quad (4.1.34)$$

For rotation with an angular velocity Ω we have

$$\mathcal{H}(\varepsilon z, -\Omega) = \mathcal{H}(z, \Omega).$$

Under the condition (4.1.34) the considerations of Sects. 3.2.1–4 will be valid only if appropriate changes are made, namely, the time reversal transformation must be accompanied by a change in sign of the magnetic field. Instead of (3.2.30) we now have the equation

$$L_{eB', \varepsilon B}(-\mathbf{H})w(\varepsilon B|-\mathbf{H}) = L_{BB'}(\mathbf{H})w(B'|\mathbf{H}),$$

and instead of (3.2.50) the generating equation becomes

$$R(y + x, x, \mathbf{H}) = R(-\varepsilon y, \varepsilon x, -\mathbf{H}). \quad (4.1.35)$$

If we proceed from (4.1.35) instead of (3.2.50), calculations analogous to those of Sects. 4.1.1, 2 can be carried out. As is easily seen, the only difference is the change in sign of the magnetic field in the terms containing ε_α . Instead of (4.1.13, 16) we get

$$\begin{aligned} l_{\beta, \alpha}(\mathbf{H}) &= \varepsilon_\alpha \varepsilon_\beta l_{\alpha, \beta}(-\mathbf{H}), \\ l_{\beta\gamma, \alpha}(\mathbf{H}) &= kT[\varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma l_{\alpha, \beta\gamma}(-\mathbf{H}) - l_{\beta, \alpha\gamma}(\mathbf{H}) - l_{\gamma, \alpha\beta}(\mathbf{H})]. \end{aligned} \quad (4.1.36)$$

One should make analogous changes in the other FDRs. No changes need be made in the formula (4.1.12) which follows simply from dynamic equilibrium. If the Hamiltonian function depends upon other time-odd external parameters, these must be substituted for \mathbf{H} in (4.1.36) and in other relations.

4.1.5 The Functions R_+ and R_- and Their Relationship

From the above considerations we see that the relations obtained by differentiating (4.1.3) at the zero point partly duplicate each other, i.e. not all relations are independent of one another. To obtain only independent relations one should change the method of derivation.

Let us introduce the auxiliary functions

$$2R_\pm(y, x) = R(y, x) \pm R(-\varepsilon y, \varepsilon x). \quad (4.1.37)$$

From (4.1.37) it follows that

$$\begin{aligned} R(y, x) &= R_+(y, x) + R_-(y, x), \\ R(-\varepsilon y, \varepsilon x) &= R_+(y, x) - R_-(y, x). \end{aligned} \quad (4.1.38)$$

Substituting (4.1.38) into (3.2.46) gives

$$[\exp(x\partial/\partial y) + 1]R_-(y, x) = -[\exp(x\partial/\partial y) - 1]R_+(y, x). \quad (4.1.39)$$

Operating on both sides of (4.1.39) by $[\exp(x\partial/\partial y) + 1]^{-1}$, we have

$$R_-(y, x) = -\tanh(\frac{1}{2}x\partial/\partial y)R_+(y, x). \quad (4.1.40)$$

This equation is one of the forms of the generating equation. We see that the odd part R_- of the image is completely determined by the even part R_+ . The function $\tanh(z/2)$ in (4.1.33) can be represented as

$$\tanh(z/2) = \sum_{j=0}^{\infty} c_{2j+1} z^{2j+1}, \quad (4.1.41)$$

where

$$c_{2j+1} = 2 \frac{2^{2j+2} - 1}{(2j+2)!} B_{2j+2}. \quad (4.1.42)$$

Here B_{2j+2} are the Bernoulli numbers. The first three coefficients of (4.1.41) are

$$c_1 = \frac{1}{2}, \quad c_3 = -\frac{1}{24}, \quad c_5 = \frac{1}{240}. \quad (4.1.43)$$

Substituting (3.1.41) into the right-hand side of (4.1.37) yields

$$\begin{aligned} R_{\pm}(y, x) &= \frac{1}{2} \sum_{m=1}^{\infty} \frac{1}{m!} \beta^{m-1} [\kappa_{\alpha_1 \dots \alpha_m}(x) \\ &\quad \pm (-1)^m \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \kappa_{\alpha_1 \dots \alpha_m}(\varepsilon x)] y_{\alpha_1} \dots y_{\alpha_m}. \end{aligned} \quad (4.1.44)$$

If we now substitute (4.1.44) into (4.1.40), consider (4.1.41) and select the terms of order y^m , we shall obtain the equations replacing (4.1.3). On their left-hand sides the expressions will be identical, but on the right-hand side the series with coefficients c_{2j+1} will appear in place of the series with coefficients $1/l!$.

4.1.6 Another Form of Many-Subscript Relations

If we differentiate the above-mentioned equations with respect to x at the zero point several times, we shall obtain a new system of many-subscript relations which does not contain the duplication. They can also be derived in a different way.

Considering (4.1.6) and using the Taylor expansion of $\kappa_{\alpha_1 \dots \alpha_m}$, we can write (4.1.44) as

$$\begin{aligned} R_{\pm}(y, x) &= \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} \frac{1}{m! n!} \beta^{m-1} 2^{-1} [1 \pm (-1)^m \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \varepsilon_{\beta_1} \dots \varepsilon_{\beta_n}] \\ &\quad \times l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} y_{\alpha_1} \dots y_{\alpha_m} x_{\beta_1} \dots x_{\beta_n} \end{aligned} \quad (4.1.45)$$

or

$$R_+(y, x) = U_+ R(y, x), \quad R_-(y, x) = U_- R(y, x). \quad (4.1.46)$$

Here U_+ is an operator that selects out the terms for which

$$(-1)^m \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \varepsilon_{\beta_1} \dots \varepsilon_{\beta_n} = 1 \quad (4.1.47)$$

and omits the other terms; U_- selects out the terms with

$$(-1)^m \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \varepsilon_{\beta_1} \dots \varepsilon_{\beta_n} = -1. \quad (4.1.48)$$

Substituting (4.1.46) into (4.1.40) yields

$$U_- R(y, x) = - \tanh(2^{-1} x \partial/\partial y) U_+ R(y, x). \quad (4.1.49)$$

If we analyse the operation of $x(\partial/\partial y)U_+$ and $U_- x \partial/\partial y$ on series of powers of x and y , we easily verify that

$$(x \partial/\partial y) U_+ = U_- x \partial/\partial y, \quad (x \partial/\partial y)^2 U_+ = U_+ (x \partial/\partial y)^2 \quad (4.1.50)$$

and, consequently,

$$\tanh(2^{-1} x \partial/\partial y) U_+ = U_- \tanh(2^{-1} x \partial/\partial y). \quad (4.1.51)$$

By virtue of (4.1.51), equation (4.1.49) takes the form

$$U_- [R(y, x) + \tanh(2^{-1} x \partial/\partial y) R(y, x)] = 0. \quad (4.1.52)$$

Now consider the action of the operator $x \partial/\partial y$ on the series

$$F = \sum_{m,n} \frac{\beta^m}{m! n!} b_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} y_{\alpha_1} \dots y_{\alpha_m} x_{\beta_1} \dots x_{\beta_n} \quad (4.1.53)$$

in detail. We have

$$x_\gamma \partial F / \partial y_\gamma = \sum_{m,n} \frac{\beta^m}{(m-1)! n!} b_{\alpha_1 \dots \alpha_{m-1}, \gamma, \beta_1 \dots \beta_n} y_{\alpha_1} \dots y_{\alpha_{m-1}} x_{\beta_1} \dots x_{\beta_n} x_\gamma. \quad (4.1.54)$$

We write the last series in the form

$$\sum \frac{1}{k! l!} \beta^k \tilde{b}_{\alpha_1 \dots \alpha_k, \beta_1 \dots \beta_l} y_{\alpha_1} \dots y_{\alpha_k} x_{\beta_1} \dots x_{\beta_l}, \quad (4.1.55)$$

where $\tilde{b}_{\alpha_1 \dots \alpha_k, \beta_1 \dots \beta_l}$ is taken to be symmetrical with respect to the subscripts $\alpha_1, \dots, \alpha_k$ and also with respect to the subscripts β_1, \dots, β_l . Comparing the expressions on the right-hand sides of (4.1.54, 55) at $k = m - 1$ and $l = n + 1$, we obtain

$$\tilde{b}_{\alpha_1 \dots \alpha_k, \beta_1 \dots \beta_l} = \beta \sum_{i=1}^l b_{\alpha_1 \dots \alpha_k \beta_i, \beta_1 \dots \beta_{i-1} \beta_{i+1} \dots \beta_l}. \quad (4.1.56)$$

We will treat (4.1.56) as the result of the action of an operator Q which transposes $b_{\alpha_1 \dots \alpha_{k+1}, \beta_1 \dots \beta_{l-1}}$ into $\tilde{b}_{\alpha_1 \dots \alpha_k, \beta_1 \dots \beta_l}$:

$$\tilde{b}_{\alpha_1 \dots \alpha_k, \beta_1 \dots \beta_l} = Q b_{\alpha_1 \dots \alpha_{k+1}, \beta_1 \dots \beta_{l-1}}. \quad (4.1.57)$$

Then as a consequence of (4.1.56) we have

$$(Qb)_{\alpha_1 \dots \alpha_k, \beta_1 \dots \beta_l} = \beta \sum_{i=1}^l b_{\alpha_1 \dots \alpha_k \beta_i, \beta_1 \dots \beta_{i-1} \beta_{i+1} \dots \beta_l}. \quad (4.1.58)$$

This formula shows the action of the operator Q . Thus, we see that the action of the operator $x\partial/\partial y$ on a series F is equivalent to the action of the operator Q on the coefficients of the series. This equivalence is used after inserting

$$R(y, x) = \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} \frac{1}{m! n!} \beta^{m-1} l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} y_{\alpha_1} \dots y_{\alpha_m} x_{\beta_1} \dots x_{\beta_n} \quad (4.1.59)$$

into (4.1.52). Taking into account that U_- selects the terms with property (4.1.48), we obtain

$$l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} = -(\tanh(\frac{1}{2}Q)l)_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} \quad (4.1.60)$$

or, according to (4.1.41),

$$l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} = - \sum_{i \geq 0} c_{2j+1} Q^{2j+1} l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} \quad (4.1.61)$$

at

$$(-1)^m \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \varepsilon_{\beta_1} \dots \varepsilon_{\beta_n} = -1. \quad (4.1.62)$$

The number of terms on the right-hand side of (4.1.61) is finite. From (4.1.58) we see that the action of the operator Q decreases the number of subscripts appearing to the right of the comma. This number cannot be negative. For this reason $Q^{2j+1} l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} = 0$ for $2j+1 > n$. The number of terms in (4.1.61) is equal to the integer part of $(n+1)/2$.

Formula (4.1.61) is the desired new form of the many-subscript relations. In particular, using (4.1.43, 58, 62), we have

$$l_{\alpha_1 \dots \alpha_m} = 0 \quad \text{for} \quad \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} = (-1)^{m+1}, \quad m = 1, 2, \dots, \quad (4.1.63)$$

$$l_{\alpha_1 \dots \alpha_m \beta} = -2kT l_{\alpha_1 \dots \alpha_m, \beta} \quad \text{for} \quad \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \varepsilon_{\beta} = (-1)^{m+1}, \quad m = 0, 1, \dots, \quad (4.1.64)$$

$$\begin{aligned} l_{\alpha_1 \dots \alpha_m \beta, \gamma} + l_{\alpha_1 \dots \alpha_m \gamma, \beta} &= -2kT l_{\alpha_1 \dots \alpha_m, \beta \gamma} \\ \text{for} \quad \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_m} \varepsilon_{\beta} \varepsilon_{\gamma} &= (-1)^{m+1}, \quad m = 0, 1, \dots. \end{aligned} \quad (4.1.65)$$

These relations correspond to the values $n = 0, n = 1, n = 2$, respectively. All these relations and the others derived from (4.1.61) are independent. Using them one can also obtain the basic two-, three- and four-subscript FDRs found in Sect. 4.1.2.

4.2 Approximate Markov FDRs and Their Covariant Form

4.2.1 Approximate Relationship Between the Coefficient Function and Its Image

The Markov FDRs obtained in the previous section from the generating equation are exact. The disadvantage of these FDRs is that they include the derivatives of the images $\kappa_{\alpha_1 \dots \alpha_n}(x)$ of the coefficient functions $K_{\alpha_1 \dots \alpha_n}(B)$, but not the derivatives of

the coefficient functions themselves. In this section we derive FDRs containing the derivatives of $K_{\alpha_1 \dots \alpha_n}(B)$ although, perforce, these FDRs are approximate (or asymptotic). Their validity is conditioned by the smallness of k .

The functions $\kappa_{\alpha_1 \dots \alpha_n}(x)$ and $K_{\alpha_1 \dots \alpha_n}(B)$ are related by (3.1.42). Let us derive simpler, but approximate formulas from (3.1.42). We denote $m_\alpha(x) = \langle B_\alpha \rangle_x$, i.e.

$$m_\alpha(x) = \int B_\alpha w_x(B) dB$$

and $\Delta B_\alpha = B_\alpha - m_\alpha(x)$. Furthermore, (3.1.42) can be written as

$$\kappa_{\alpha_1 \dots \alpha_n}(x) = \langle K_{\alpha_1 \dots \alpha_n}(m + \Delta B) \rangle_x .$$

Expanding $K_{\alpha_1 \dots \alpha_n}$ in ΔB , we obtain

$$\begin{aligned} \kappa_{\alpha_1 \dots \alpha_n}(x) &= \left\langle K_{\alpha_1 \dots \alpha_n}[m(x)] + \frac{\partial K_{\alpha_1 \dots \alpha_n}(m)}{\partial B_\beta} \Delta B_\beta \right. \\ &\quad \left. + \frac{1}{2} \frac{\partial^2 K_{\alpha_1 \dots \alpha_n}(m)}{\partial B_\beta \partial B_\gamma} \Delta B_\beta \Delta B_\gamma + \dots \right\rangle_x . \end{aligned}$$

But $\langle \Delta B \rangle_x = 0$. Consequently, we have

$$\kappa_{\alpha_1 \dots \alpha_n}(x) = K_{\alpha_1 \dots \alpha_n}[m(x)] + \frac{1}{2} \frac{\partial^2 K_{\alpha_1 \dots \alpha_n}(m)}{\partial B_\beta \partial B_\gamma} \langle \Delta B_\beta \Delta B_\gamma \rangle + \dots . \quad (4.2.1)$$

We introduce a function $\Phi(x)$ by an equation similar to (2.2.86):

$$\exp[-\beta\Phi(x)] = \int \exp[\beta x B - \beta F(B)] dB . \quad (4.2.2)$$

We can easily verify that formulas analogous to (2.2.30) are valid:

$$\begin{aligned} \langle B_\alpha \rangle_x &\equiv m_\alpha(x) = -\frac{\partial \Phi(x)}{\partial x_\alpha} , \\ \langle \Delta B_\alpha \Delta B_\beta \rangle_x &\equiv \langle B_\alpha, B_\beta \rangle_x = -kT \frac{\partial^2 \Phi(x)}{\partial x_\alpha \partial x_\beta} , \\ \langle B_\alpha, B_\beta, B_\gamma \rangle_x &= -(kT)^2 \frac{\partial^3 \Phi(x)}{\partial x_\alpha \partial x_\beta \partial x_\gamma} , \\ &\vdots \end{aligned} \quad (4.2.3)$$

When (3.1.43) holds, the function $\Phi(x)$ is expressed in terms of $F(a)$: $\Phi(x) = F(a^0 + x)$ [(3.1.46) is used]. Then (4.2.3) coincides with (2.2.30) at $m = 1, 2, 3$. However, (4.2.3) remains valid even when (3.1.43) is invalid.

Substituting (4.2.3) into (4.2.1) gives

$$\kappa_{\alpha_1 \dots \alpha_n}(x) = K_{\alpha_1 \dots \alpha_n} \left(-\frac{\partial \Phi(x)}{\partial x} \right) - \frac{1}{2} kT \frac{\partial^2 K_{\alpha_1 \dots \alpha_n}}{\partial B_\beta \partial B_\gamma} \left(-\frac{\partial \Phi}{\partial x} \right) \frac{\partial^2 \Phi(x)}{\partial x_\beta \partial x_\gamma} + \dots . \quad (4.2.4)$$

We also introduce a function $G(x)$ as the Legendre transform of the function $F(A)$:

$$G(x) = F[A(x)] - xA(x) . \quad (4.2.5)$$

Here $A(x)$ is the inverse dependence of the dependence $x_\alpha = \partial F(A)/\partial A_\alpha$. Differentiating (4.2.5), we readily obtain

$$A_\alpha(x) = -\partial G(x)/\partial x_\alpha. \quad (4.2.6)$$

According to the results of Appendix 1, where the substitution $\kappa = \beta^{-1}$, $\Psi(B) = F(B)$ must be made, we have

$$\Phi(x) - G(x) = \mathcal{O}(k). \quad (4.2.7)$$

Therefore, from (4.2.4) we find

$$\kappa_{\alpha_1 \dots \alpha_n}(x) = K_{\alpha_1 \dots \alpha_n}(-\partial G(x)/\partial x)[1 + \mathcal{O}(k)]. \quad (4.2.8)$$

If we want to obtain a more precise relation, we must take into account the term with the second derivative in (4.2.4) and also consider the difference $\Phi(x) - G(x)$ in the first order in k . By virtue of (A4.1) we have

$$d\Phi = dG + \frac{1}{2} kTF_{\alpha\beta}^{-1} dF_{\alpha\beta} + \mathcal{O}(k)^2. \quad (4.2.9)$$

Here $F_{\alpha\beta} = \partial^2 F/\partial B_\alpha \partial B_\beta$ at $B = A(x)$. Since, by virtue of (4.2.6), the equation $F_{\alpha\beta} = -G_{\alpha\beta}^{-1}$ is valid, where $G_{\alpha\beta} = \partial^2 G/\partial x_\alpha \partial x_\beta$, by differentiation we obtain

$$dF_{\alpha\beta} = G_{\beta\gamma}^{-1} dG_{\gamma\delta} G_{\delta\alpha}^{-1}. \quad (4.2.10)$$

Consequently, (4.2.9) gives

$$\partial\Phi/\partial x_\sigma = \partial G/\partial x_\sigma - \frac{1}{2} kTG_{\alpha\sigma\delta} G_{\delta\alpha}^{-1}, \quad (4.2.11)$$

where $G_{\alpha\sigma\delta} = \partial^3 G/\partial x_\alpha \partial x_\sigma \partial x_\delta$. Now, from (4.2.4) we can easily find a more precise relation:

$$\begin{aligned} \kappa_{\alpha_1 \dots \alpha_n}(x) &= \left[K_{\alpha_1 \dots \alpha_n} \left(-\frac{\partial G}{\partial x} \right) + \frac{1}{2} kT \frac{\partial K_{\alpha_1 \dots \alpha_n}}{\partial B_\beta} G_{\beta\alpha} G_{\alpha\delta}^{-1} \right. \\ &\quad \left. - \frac{1}{2} kT \frac{\partial^2 K_{\alpha_1 \dots \alpha_n}}{\partial B_\beta \partial B_\gamma} G_{\beta\gamma} \right] [1 + \mathcal{O}(k^2)], \end{aligned} \quad (4.2.12)$$

the derivatives of $K_{\alpha_1 \dots \alpha_n}$ being taken at $B = -\partial G(x)/\partial x$. We shall not consider more precise formulas.

4.2.2 Markov FDRs in Zeroth and First Orders in k

In order to obtain approximate Markov FDRs in zeroth order in k , i.e. the least precise FDRs, we must find the derivatives of the functions (4.2.8) with respect to x at the zero point and insert them into the precise Markov FDRs obtained in Sect. 4.1. Let us denote the point of the minimum of free energy $F(B)$ by B^0 , then $B = B^0$ corresponds to $x = 0$, i.e. $\partial F/\partial B = 0$.

In the given approximation, the one-subscript equation (4.1.10) takes the form

$$K_\alpha(B^0) = 0. \quad (4.2.13)$$

The two-subscript or linear FDRs (4.1.12, 13) can be written as

$$K_{\alpha\beta} = -kT \left(\frac{\partial K_\alpha}{\partial B_\gamma} F_{\gamma\beta}^{-1} + \frac{\partial K_\beta}{\partial B_\gamma} F_{\gamma\alpha}^{-1} \right), \quad (4.2.14a)$$

$$\frac{\partial K_\alpha}{\partial B_\gamma} F_{\gamma\beta}^{-1} = \varepsilon_\alpha \varepsilon_\beta \frac{\partial K_\beta}{\partial B_\gamma} F_{\gamma\alpha}^{-1} \quad \text{at } B = B^0. \quad (4.2.14b)$$

We have taken into account that $G_{\gamma\beta} = -F_{\gamma\beta}^{-1}$. Here we write down only one three-subscript or quadratic relation:

$$K_{\alpha\beta\gamma} = (kT)^2 (1 - \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma) P_{(\alpha\beta\gamma)} \left[\frac{\partial^2 K_\alpha}{\partial B_\rho \partial B_\sigma} G_{\rho\beta} G_{\sigma\gamma} - \frac{\partial K_\alpha}{\partial B_\rho} G_{\rho\beta\gamma} \right] \\ \text{at } B = B^0, x = 0, \quad (4.2.15)$$

which follows from (4.1.18). Here $P_{(\alpha\beta\gamma)}$ denotes the sum of the terms obtained by cyclic permutations of the subscripts α, β, γ . The expressions

$$K_{\alpha\beta\gamma}, \quad -\frac{\partial K_{\alpha\beta}}{\partial B_\rho} G_{\rho\gamma}, \quad \frac{\partial^2 K_\alpha}{\partial B_\rho \partial B_\sigma} G_{\rho\beta} G_{\sigma\gamma} - \frac{\partial K_\alpha}{\partial B_\sigma} G_{\sigma\beta\gamma} \quad (4.2.16)$$

taken at $B = B^0, x = 0$ must respectively replace the terms $l_{\alpha\beta\gamma}, l_{\alpha\beta,\gamma}, l_{\alpha,\beta\gamma}$ appearing in the precise three-subscript relations.

In the four-subscript or cubic case the expressions

$$K_{\alpha\beta\gamma\delta}, \quad (4.2.17a)$$

$$-\frac{\partial K_{\alpha\beta\gamma}}{\partial B_\rho} G_{\rho\delta}, \quad (4.2.17b)$$

$$\frac{\partial^2 K_{\alpha\beta}}{\partial B_\rho \partial B_\sigma} G_{\rho\gamma} G_{\sigma\delta} - \frac{\partial K_{\alpha\beta}}{\partial B_\sigma} G_{\sigma\gamma\delta}, \quad (4.2.17c)$$

$$-\frac{\partial^3 K_\alpha}{\partial B_\rho \partial B_\sigma \partial B_\tau} G_{\rho\beta} G_{\sigma\gamma} G_{\tau\delta} + P_{(\beta\gamma\delta)} \frac{\partial^2 K_\alpha}{\partial B_\rho \partial B_\sigma} G_{\rho\beta} G_{\sigma\gamma\delta} - \frac{\partial K_\alpha}{\partial B_\sigma} G_{\sigma\beta\gamma\delta} \quad (4.2.17d)$$

taken at $B = B^0$ must in turn replace the matrices $l_{\alpha\beta\gamma\delta}, l_{\alpha\beta\gamma,\delta}, l_{\alpha\beta,\gamma\delta}, l_{\alpha,\beta\gamma\delta}$ in the precise FDRs.

Considering (4.2.12), instead of (4.2.8) we can obtain more precise FDRs. We give only one of them, namely, the relation that is more precise than (4.2.13). By virtue of (4.2.12), we have from (4.1.10)

$$K_\alpha + \frac{1}{2} kT \frac{\partial K_\alpha}{\partial B_\beta} G_{\beta\alpha\delta} G_{\alpha\delta}^{-1} - \frac{1}{2} kT \frac{\partial^2 K_\alpha}{\partial B_\rho \partial B_\gamma} G_{\beta\gamma} = 0, \quad \text{at } B = B^0, \quad (4.2.18)$$

which must replace (4.2.13) if more accuracy is needed.

We note that in (4.2.15–18) it is advisable to express the derivatives $G_{\alpha\beta}, G_{\alpha\beta\gamma}, G_{\alpha\beta\gamma\delta}$ in terms of the free energy $F(B)$. In order to do this one should use the equation $G_{\alpha\beta} = -F_{\alpha\beta}^{-1}$ and equations

$$G_{\alpha\beta\gamma} = F_{\alpha\rho}^{-1} F_{\beta\sigma}^{-1} F_{\gamma\tau}^{-1} F_{\rho\sigma\tau}, \quad (4.2.19a)$$

$$G_{\alpha\beta\gamma\delta} = F_{\alpha\rho}^{-1} F_{\beta\sigma}^{-1} F_{\gamma\tau}^{-1} F_{\delta\pi}^{-1} (F_{\rho\sigma\tau\pi} - P_{(\rho\sigma\tau\pi)} F_{\rho\sigma\mu} F_{\mu\nu}^{-1} F_{\nu\tau\pi}) \quad (4.2.19b)$$

obtained from the earlier one by single and double differentiation with respect to x . Here $F_{\rho\sigma\tau} = \partial^3 F(B) / \partial B_\rho \partial B_\sigma \partial B_\tau$ and an analogous relation exists for $F_{\rho\sigma\tau\pi}$.

4.2.3 The Covariant Form of One-Subscript and Two-Subscript FDRs

All general formulas and relations of nonequilibrium thermodynamics are covariant under linear transformations, and the thermodynamic forces $x = (x_\alpha)$ must be covariant vectors if we assume that the internal parameters $B = (B^\alpha)$ are contravariant. We are now interested in the more complex question of whether the Markov FDRs are covariant under arbitrary curvilinear transformations when the metric tensor $g_{\alpha\beta}(B)$ is given. If the covariance exists, we can use the FDRs corresponding to the case when the parameters B^α are coordinates of curvilinear space. Further, we show that one-, two-, three- and four-subscript FDRs can be written in the tensor-covariant form.

It should be noted that the precise generating equation (3.2.50) and the precise FDRs considered in Sect. 4.1.2 are not covariant under curvilinear transformations for the following reasons. The fact is that they have been derived by using integration, which violates covariance under curvilinear transformations. Moreover, the basic equation (3.2.30) is noncovariant.

Only the approximate or asymptotic FDRs whose validity is conditioned by the smallness of k can be covariant. Owing to the smallness of k , the one-time equilibrium probability density is concentrated in only a very small vicinity of the equilibrium point. Due to this fact, there is practically no spreading over space, and local transformation properties of vectors and tensors become important.

From (2.3.30, 34), where D^α is a contravariant vector, we see that, strictly speaking, $K^\alpha(B)$ has no vector transformation properties. However, since $K^{\alpha\beta} \sim k$, $K^{\alpha\beta\gamma} \sim k^2$, the functions K^α approximately form a vector to zeroth order in k . Therefore, equation (4.2.13) or, more correctly, the equation

$$K^\alpha(B^0) = 0, \quad (4.2.20)$$

which is valid in zeroth order in k , is approximately covariant under curvilinear transformations.

We now proceed to two-subscript relations (4.2.14). It is seen from (2.3.34) that $K^{\alpha\beta}(B)$ can be regarded as a tensor of second rank with relative error of the order of k . In general, all coefficient functions $K^{\alpha_1 \dots \alpha_n}$ are tensors with this relative error. The expression $(\partial K^\alpha / \partial B^\beta) F_{\gamma\beta}^{-1}$ remains to be considered. As is well known [4.1, 2], covariant derivatives of vectors are written as

$$\begin{aligned} (K^\alpha)_{;\gamma} &= \partial K^\alpha / \partial B^\gamma + \Gamma_{\gamma\sigma}^\alpha K^\sigma, \\ (\partial F / \partial B^\beta)_{;\gamma} &= \partial^2 F / \partial B^\gamma \partial B^\beta - \Gamma_{\beta\gamma}^\sigma (\partial F / \partial B^\sigma). \end{aligned} \quad (4.2.21)$$

But the terms with the Christoffel symbols $\Gamma_{\gamma\sigma}^\alpha$ drop out at point B^0 by virtue of (4.2.20) and the relation

$$\partial F(B) / \partial B^\beta = 0 \quad \text{at } B = B^0, \quad (4.2.22)$$

which is a consequence of the condition of extremum of the function $F(B)$ at the point B^0 . Therefore,

$$\begin{aligned} (K^\alpha)_{;\gamma} &= \partial K^\alpha / \partial B^\gamma, \\ (\partial F / \partial B^\beta)_{;\gamma} &= \partial^2 F / \partial B^\gamma \partial B^\beta \quad \text{at } B = B^0. \end{aligned} \quad (4.2.23)$$

Hence, (4.2.14) can be written as

$$K^{\alpha\beta} = -kT[(K^\alpha)_{;\gamma}r^{\gamma\beta} + (K^\beta)_{;\gamma}r^{\gamma\alpha}], \quad (4.2.24a)$$

$$(K^\alpha)_{;\gamma}r^{\gamma\beta} = \varepsilon_\alpha \varepsilon_\beta (K^\beta)_{;\gamma}r^{\gamma\alpha} \quad \text{at } B = B^0 \quad (4.2.24b)$$

(there is no summation over α, β). Here

$$\|r^{\gamma\beta}\| = \|(\partial F/\partial B^\beta)_{;\gamma}\|^{-1}. \quad (4.2.25)$$

The covariance of the relations (4.2.22, 24) means that these relations remain, in essence, unchanged when the coordinate system changes. The numerical values of the quantities appearing in these relations differ in various coordinate systems only because the same relations “are seen from different points of view in different coordinate systems”.

4.2.4 The Covariant Form of Quadratic FDRs

Proceeding to quadratic FDRs, we take as an example the FDR (4.2.15), which, by virtue of (4.2.19a), takes the form

$$\begin{aligned} K^{\alpha\beta\gamma} &= (kT)^2(1 - \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma)P_{(\alpha\beta\gamma)} \\ &\times \left[\frac{\partial^2 K^\alpha}{\partial B^\sigma \partial B^\rho} F_{\rho\beta}^{-1} F_{\sigma\gamma}^{-1} - \frac{\partial K^\alpha}{\partial B^\rho} F_{\rho\sigma}^{-1} F_{\sigma\tau\pi} F_{\tau\beta}^{-1} F_{\pi\gamma}^{-1} \right] \quad \text{at } B = B^0. \end{aligned} \quad (4.2.26)$$

Here contravariant indices are written as superscripts in contrast to (4.2.15). Let us consider the covariant derivatives $((K^\alpha)_{;\rho})_{;\sigma}$, $((F_\sigma)_{;\tau})_{;\pi}$ ($F_\sigma = \partial F/\partial B^\sigma$). Differentiating the tensors (4.2.21) with the help of the covariant derivative formulas and using (4.2.20, 22), we easily obtain

$$\begin{aligned} ((K^\alpha)_{;\rho})_{;\sigma} &= \frac{\partial^2 K^\alpha}{\partial B^\sigma \partial B^\rho} + \Gamma_{\rho\nu}^\alpha \frac{\partial K^\nu}{\partial B^\sigma} + \Gamma_{\sigma\nu}^\alpha \frac{\partial K^\nu}{\partial B^\rho} - \Gamma_{\rho\sigma}^\nu \frac{\partial K^\alpha}{\partial B^\nu}, \\ ((F_\sigma)_{;\tau})_{;\pi} &= F_{\sigma\tau\pi} - \Gamma_{\sigma\tau}^\mu F_{\mu\pi} - \Gamma_{\sigma\pi}^\mu F_{\mu\tau} - \Gamma_{\tau\pi}^\mu F_{\mu\sigma} \end{aligned} \quad (4.2.27)$$

at $B = B^0$. Here the terms with $\Gamma_{\rho\nu}^\alpha$ do not drop out; therefore, $\partial^2 K^\alpha/\partial B^\sigma \partial B^\rho$ and $F_{\sigma\tau\pi}$ do not coincide with the covariant derivatives. This means that the relation (4.2.26) is not covariant and that it is really different in the various coordinate systems, i.e. different not only because it is “seen from different points of view in different coordinate systems”.

In order to obtain the covariant relation we introduce a special coordinate system, namely, the locally-geodesic coordinate system, i.e. a system in which the Christoffel symbols are equal to zero at the equilibrium point B^0 . Let the Christoffel symbols be equal to $\Gamma_{\beta\gamma}^\alpha(B)$ in the initial coordinate system with coordinates B . In the new coordinate system with coordinates B' they are equal to

$$\Gamma'^\alpha_{\rho\tau} = \Gamma_{\beta\gamma}^\alpha \frac{\partial B'^\sigma}{\partial B^\alpha} \frac{\partial B^\beta}{\partial B'^\rho} \frac{\partial B^\gamma}{\partial B'^\tau} + \frac{\partial^2 B^\alpha}{\partial B'^\rho \partial B'^\sigma} \frac{\partial B'^\sigma}{\partial B^\alpha}, \quad (4.2.28)$$

as is well known [4.1, 2].

If we introduce the new coordinate system with coordinates B' by

$$B^\alpha = B'^\alpha - 1/2 \Gamma_{\rho\sigma}^\alpha(B^0)(B' - B'^0)^\rho(B' - B'^0)^\sigma + \mathcal{O}(B' - B'^0)^3, \quad (4.2.29)$$

then, as it is easily seen from (4.2.28), in the new coordinate system we have

$$\Gamma'_{\rho\tau}^\sigma = 0 \quad \text{at } B' = B'^0 = B'(B^0). \quad (4.2.30)$$

Owing to this relation and by virtue of (4.2.27) $\partial^2 K'^\alpha / \partial B'^\sigma \partial B'^\rho$ and $\partial^3 F / \partial B'^\sigma \partial B'^\tau \partial B'^\pi$ coincide with $((K'^\alpha);_\sigma)_\rho$ and $((\partial F / \partial B'^\alpha);_\tau)_\pi$ at the point $B' = B'^0$ in the new coordinate system. Therefore, the relation (4.2.26) can be written in the form

$$K'^{\alpha\beta\gamma} = (kT)^2 (1 - \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma) P_{(\alpha\beta\gamma)} [((K'^\alpha);_\rho)_\sigma - (K'^\alpha);_\mu r'^{\mu\nu} F_{\nu\rho\sigma}] r'^\rho{}^\beta r'^\sigma{}^\gamma \quad (4.2.31)$$

at $B' = B'(B^0)$, where the tensor $r'^{\mu\nu}$ has the same sense as in (4.2.24). If we now switch over to an arbitrary coordinate system, then we shall have the relation

$$K^{\alpha\beta\gamma} = (kT)(1 - \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma) P_{(\alpha\beta\gamma)} [((K^\alpha);_\rho)_\sigma - (K^\alpha);_\mu r^{\mu\nu} F_{\nu\rho\sigma}] r^{\rho\beta} r^{\sigma\gamma} \quad (4.2.32)$$

i.e. the covariant relation.

The above derivation of the covariant FDR consists in the following: from all essentially different subvarieties of relation that are due to noncovariance of (4.2.26) we select the subvariety corresponding to the geodesic coordinate system, and then we "look at this subvariety from different points of view", i.e. in different coordinate systems.

By virtue of (4.2.30) we also have $(K'^{\alpha\beta})_{,\rho} = \partial K'^{\alpha\beta} / \partial B'^\rho$ at $B' = B'^0$. If we take this fact and what has been said above into consideration, we can formulate the rule of transformation to the covariant form for an arbitrary three-subscript relation: one should make the substitutions

$$\begin{aligned} l_{\alpha\beta\gamma} &\rightarrow K^{\alpha\beta\gamma}, & l_{\alpha\beta,\gamma} &\rightarrow (K^{\alpha\beta})_{,\rho} r^{\rho\gamma}, \\ l_{\alpha,\beta\gamma} &\rightarrow [((K^\alpha);_\rho)_\sigma - (K^\alpha);_\mu r^{\mu\nu} ((F_\nu);_\rho)_\sigma] r^{\rho\beta} r^{\sigma\gamma} \end{aligned} \quad (4.2.33)$$

into the precise relations [cf. (4.2.16)].

The geodesic coordinate system can also be introduced in order to write down the relation (4.2.18), which is more precise than (4.2.20), in the covariant form. In (4.2.18) we have taken into account the quantities of first order in the small parameter k . Therefore, we cannot regard K^α as a vector in this relation, but we can regard the expression $K^\alpha + 1/2 \Gamma_{\beta\gamma}^\alpha K^{\beta\gamma}$ as a vector, as is seen from (2.3.37) and from the estimation $K^{\alpha\beta\gamma} \sim k^2$. Since the additional term $1/2 \Gamma_{\beta\gamma}^\alpha K^{\beta\gamma}$ drops out in the geodesic coordinate system, after transformation to an arbitrary coordinate system we can simply add it to the relation sought for. Taking into consideration also all that has been said above, we transform (4.2.18) to the covariant form:

$$\begin{aligned} K^\alpha + 1/2 \Gamma_{\beta\gamma}^\alpha K^{\beta\gamma} - 1/2 kT (K^\alpha);_\mu r^{\mu\nu} ((F_\nu);_\sigma)_\tau r^{\sigma\tau} + 1/2 kT ((K^\alpha);_\beta)_\gamma r^{\beta\gamma} &= 0 \\ \text{at } B = B^0. \end{aligned} \quad (4.2.34)$$

4.2.5 The Covariant Form of Cubic FDRs

As pointed out in Sect. 4.2.2, in order to obtain the cubic FDRs that hold in zeroth order in k from exact FDRs, one should replace $l_{\alpha\beta\gamma\delta}$, $l_{\alpha\beta\gamma,\delta}$, $l_{\alpha\beta,\gamma\delta}$, $l_{\alpha,\beta\gamma\delta}$, respectively, by the expressions (4.2.17) in which the contravariant indices should be written as superscripts. The first of these expressions, $K^{\alpha\beta\gamma\delta}$, already has tensor transformation properties in the frame of the required accuracy. Going to (4.2.17b), let us consider the covariant derivative

$$(K^{\alpha\beta\gamma})_{;\sigma} = \partial K^{\alpha\beta\gamma}/\partial B^\sigma + \Gamma_{\sigma\mu}^\alpha K^{\mu\beta\gamma} + \Gamma_{\sigma\mu}^\beta K^{\mu\alpha\gamma} + \Gamma_{\sigma\mu}^\gamma K^{\mu\alpha\beta}. \quad (4.2.35)$$

From this we see that, generally speaking, $\partial K^{\alpha\beta\gamma}/\partial B^\sigma$ is not a tensor. However, this derivative coincides with a tensor $(K^{\alpha\beta\gamma})_{;\sigma}$ in the geodesic coordinate system where $\Gamma_{\sigma\rho}^\alpha = 0$. Therefore, for obtaining the covariant FDRs one should make the substitution

$$l_{\alpha\beta\gamma,\delta} \rightarrow (K^{\alpha\beta\gamma})_{;\sigma} r^{\sigma\delta} \quad \text{at } B = B^0 \quad (4.2.36)$$

in the arbitrary coordinate system just as was done in the previous section.

We now proceed to consider the expression (4.2.17c), into which one should substitute (4.2.19). Since the derivatives $\partial^2 K^{\alpha\beta}/\partial B^\sigma \partial B^\tau$, $G_{\sigma\gamma\delta}$, $\partial K^{\alpha\beta}/\partial \beta^\sigma$ appear in (4.2.17c), one should consider the covariant derivatives $((K^{\alpha\beta})_{;\sigma})_{;\tau}$, $((F_\rho)_{;\sigma})_{;\tau}$, $(K^{\alpha\beta})_{;\sigma}$. Expressing these derivatives in terms of the Christoffel symbols and switching over to the geodesic coordinate system, we have

$$\begin{aligned} ((K^{\alpha\beta})_{;\sigma})_{;\tau} &= \frac{\partial^2 K^{\alpha\beta}}{\partial B^\sigma \partial B^\tau} + \frac{\partial \Gamma_{\sigma\mu}^\alpha}{\partial B^\tau} K^{\mu\beta} + \frac{\partial \Gamma_{\sigma\mu}^\beta}{\partial B^\tau} K^{\mu\alpha}, \\ (K^{\alpha\beta})_{;\sigma} &= \partial K^{\alpha\beta}/\partial B^\sigma, \\ ((F_\rho)_{;\sigma})_{;\tau} &= F_{\rho\sigma\tau} \quad \text{at } B = B^0. \end{aligned} \quad (4.2.37)$$

Hence, we see that derivatives of the Christoffel symbol of the type $\partial \Gamma_{\sigma\mu}^\alpha/\partial B^\tau$ prevent $\partial^2 K^{\alpha\beta}/\partial B^\sigma \partial B^\tau$ from coinciding with $((K^{\alpha\beta})_{;\sigma})_{;\tau}$. To overcome this difficulty a special approach is needed.

Let us consider the transformation from one geodesic coordinate system to another. Let the initial coordinates be B and the subsequent ones be B' . From (4.2.28) it is seen that to keep the equation $\Gamma_{\beta\gamma}^\alpha = 0$ unchanged, the condition

$$\partial^2 B^\alpha/\partial B'^\rho \partial B'^\sigma = 0 \quad \text{at } B = B^0 \quad (4.2.38)$$

must hold. Let us now find how the derivatives $\partial \Gamma_{\beta\gamma}^\alpha/\partial B^\tau$ are transformed when the transformation is carried out from one geodesic system to another. Differentiating (4.2.28) with respect to B'^π and using (4.2.38) gives

$$\frac{\partial \Gamma'_{\rho\tau}^\alpha}{\partial B'^\pi} = \frac{\partial \Gamma_{\beta\gamma}^\alpha}{\partial B^\delta} \frac{\partial B'^\sigma}{\partial B^\alpha} \frac{\partial B^\beta}{\partial B'^\rho} \frac{\partial B^\gamma}{\partial B'^\tau} \frac{\partial B^\delta}{\partial B'^\pi} + \frac{\partial^3 B^\alpha}{\partial B'^\rho \partial B'^\tau \partial B'^\pi} \frac{\partial B'^\sigma}{\partial B^\alpha} \quad \text{at } B = B^0. \quad (4.2.39)$$

Performing the cyclic permutations of the subscripts ρ, τ, π and summing over these permutations, we find

$$\begin{aligned} P_{(\rho\tau\pi)} \frac{\partial \Gamma'^\sigma_{\rho\tau}}{\partial B'^\pi} &= \left(P_{(\beta\gamma\delta)} \frac{\partial \Gamma^\alpha_{\beta\gamma}}{\partial B^\delta} \right) \frac{\partial B'^\sigma}{\partial B^\alpha} \frac{\partial B^\beta}{\partial B'^\rho} \frac{\partial B^\gamma}{\partial B'^\tau} \frac{\partial B^\delta}{\partial B'^\pi} \\ &+ \frac{3\delta^3 B^\alpha}{\partial B'^\rho \partial B'^\tau \partial B'^\pi \partial B^\alpha} \quad \text{at } B' = B'^0. \end{aligned} \quad (4.2.40)$$

One can show that a coordinate system (with coordinates B') in which the sum over cyclic permutations on the left-hand side of (4.2.40) is equal to zero exists among various geodesic coordinate systems. Let the coordinates B' be defined by

$$\begin{aligned} B^\alpha &= B'^\alpha - \frac{1}{18} \left\{ P_{(\rho\tau\pi)} \left[\frac{\partial \Gamma'^\alpha_{\rho\tau}}{\partial B'^\pi} \right]_{B' = B'^0} \right\} (B' - B'^0)^\rho \\ &\times (B' - B'^0)^\tau (B' - B'^0)^\pi + \mathcal{O}(B' - B'^0)^4. \end{aligned} \quad (4.2.41)$$

Substituting (4.2.41) into (4.2.40), we easily verify that

$$0 = P_{(\rho\tau\pi)} \frac{\partial \Gamma'^\sigma_{\rho\tau}}{\partial B'^\pi} \quad \text{at } B' = B'^0. \quad (4.2.42)$$

Let us now take the well-known Riemann curvature tensor

$$R^\alpha_{\beta\gamma\delta} = \partial \Gamma^\alpha_{\beta\delta} / \partial B^\gamma - \partial \Gamma^\alpha_{\beta\gamma} / \partial B^\delta + \Gamma^\alpha_{\mu\gamma} \Gamma^\mu_{\beta\delta} - \Gamma^\alpha_{\mu\delta} \Gamma^\mu_{\beta\gamma}. \quad (4.2.43)$$

In the geodesic coordinate system B' it takes the form

$$R'^\sigma_{\rho\tau\pi} = \partial \Gamma'^\sigma_{\rho\pi} / \partial B'^\tau - \partial \Gamma'^\sigma_{\rho\tau} / \partial B'^\pi \quad \text{at } B' = B'^0. \quad (4.2.44)$$

After the permutation $\rho \leftrightarrow \pi$ we have

$$R'^\sigma_{\pi\tau\rho} = \partial \Gamma'^\sigma_{\pi\rho} / \partial B'^\tau - \partial \Gamma'^\sigma_{\pi\tau} / \partial B'^\rho \quad \text{at } B' = B'^0. \quad (4.2.45)$$

Adding equations (4.2.42, 44, 45) gives

$$3 \frac{\partial \Gamma'^\sigma_{\rho\pi}}{\partial B'^\tau} = R'^\sigma_{\rho\tau\pi} + R'^\sigma_{\pi\tau\rho} \quad \text{at } B' = B'^0. \quad (4.2.46)$$

Thus, in the special geodesic coordinate system B' the derivative $\partial \Gamma'^\sigma_{\rho\pi} / \partial B'^\tau$ can be expressed in terms of the curvature tensor. Let us use this fact. Switching over to the special coordinate system in (4.2.37) and considering (4.2.46), we have

$$\begin{aligned} \frac{\partial^2 K'^{\rho\pi}}{\partial B'^\sigma \partial B'^\tau} &= ((K'^{\rho\pi})_{;\sigma})_{;\tau} - \frac{1}{3} (R'^\rho_{\sigma\tau\mu} + R'^\rho_{\mu\tau\sigma}) K'^{\mu\pi} \\ &- \frac{1}{3} (R'^\pi_{\sigma\tau\mu} + R'^\pi_{\mu\tau\sigma}) K'^{\mu\rho} \quad \text{at } B' = B'^0. \end{aligned} \quad (4.2.47)$$

It is useful to carry out symmetrization with respect to the subscripts σ, τ in this equation. This gives

$$\frac{\partial^2 K'^{\rho\pi}}{\partial B'^\sigma \partial B'^\tau} = \frac{1}{2} P_{\sigma\tau} \left[((K'^{\rho\pi})_{;\sigma})_{;\tau} - \frac{1}{3} R'^\rho_{\sigma\tau\mu} K'^{\mu\pi} - \frac{1}{3} R'^\pi_{\sigma\tau\mu} K'^{\mu\rho} \right] \quad \text{at } B' = B'^0, \quad (4.2.48)$$

where $P_{\sigma\tau}$ denotes the symmetrized sum of the type $P_{\sigma\tau}a_{\sigma\tau} = a_{\sigma\tau} + a_{\tau\sigma}$. The terms with $R'_{\mu\sigma}$ and $R'_{\mu\tau}$ drop out since

$$R_{\beta\sigma}^\alpha + R_{\beta\tau}^\alpha = 0. \quad (4.2.49)$$

Thus, in the special coordinate system B' the derivative $\partial^2 K'^{\rho\pi}/\partial B'^\sigma \partial B'^\tau$ is equal to the expression on the right-hand side of (4.2.48). When we make further transformations of the coordinate system, the last expression transforms covariantly and $\partial^2 K^{\alpha\beta}/\partial B^\sigma \partial B^\rho$ transforms noncovariantly.

Therefore, these two expressions become unequal. However, in an arbitrary coordinate system we shall use the covariant expression

$$\frac{1}{2} P_{\sigma\tau} [((K^{\alpha\beta})_{;\rho}),_\tau] - \frac{1}{3} P_{\alpha\beta} R_{\sigma\tau\mu}^\alpha K^{\mu\beta}]$$

instead of $\partial^2 K^{\alpha\beta}/\partial B^\sigma \partial B^\tau$. This means that in order to write down covariant four-subscript FDRs one should make the substitution

$$l_{\alpha\beta,\gamma\delta} \rightarrow \left\{ \frac{1}{2} P_{\sigma\tau} [((K^{\alpha\beta})_{;\rho}),_\tau] - \frac{1}{3} P_{\alpha\beta} R_{\sigma\tau\mu}^\alpha K^{\mu\beta} \right\} - (K^{\alpha\beta})_{;\mu} r^{\mu\nu} ((F_\nu)_{;\sigma}),_\tau \} r^\sigma r^\tau \quad (4.2.50)$$

(the last expression being taken at $B = B^0$) into the precise FDRs from Sect. 4.1.2.

It remains to consider the expression (4.2.17d) into which one should insert (4.2.19). Since this expression contains the derivatives $\partial^3 K^\alpha/\partial B^\rho \partial B^\sigma \partial B^\tau$, $F_{\rho\sigma\tau\pi} = \partial^4 F/\partial B^\rho \dots \partial B^\pi$, we can write down the corresponding covariant derivatives $((K^\alpha)_{;\rho}),_\sigma),_\tau),_\pi$. Considering (4.2.20, 22), in the geodesic coordinate system we have

$$\begin{aligned} ((K^\alpha)_{;\rho}),_\sigma),_\tau) &= \frac{\partial^3 K^\alpha}{\partial B^\rho \partial B^\sigma \partial B^\tau} + \frac{\partial \Gamma_{\rho\mu}^\alpha}{\partial B^\tau} \frac{\partial K^\mu}{\partial B^\sigma} + \frac{\partial \Gamma_{\sigma\mu}^\alpha}{\partial B^\tau} \frac{\partial K^\mu}{\partial B^\rho} \\ &\quad - \frac{\partial \Gamma_{\rho\sigma}^\mu}{\partial B^\tau} \frac{\partial K^\alpha}{\partial B^\mu} + \frac{\partial \Gamma_{\rho\mu}^\alpha}{\partial B^\sigma} \frac{\partial K^\mu}{\partial B^\tau}, \end{aligned} \quad (4.2.51a)$$

$$(((F_\rho)_{;\sigma}),_\tau),_\pi) = F_{\rho\sigma\tau\pi} - \frac{\partial \Gamma_{\rho\sigma}^\mu}{\partial B^\pi} F_{\mu\tau} - \frac{\partial \Gamma_{\rho\tau}^\mu}{\partial B^\pi} F_{\mu\sigma} - \frac{\partial \Gamma_{\sigma\tau}^\mu}{\partial B^\pi} F_{\mu\rho} - \frac{\partial \Gamma_{\rho\tau}^\mu}{\partial B^\pi} F_{\mu\pi} \quad (4.2.51b)$$

Carrying out symmetrization with respect to the subscripts ρ, σ, τ in (4.2.51a) yields

$$\begin{aligned} \frac{\partial^3 K^\alpha}{\partial B^\rho \partial B^\sigma \partial B^\tau} &= \left\{ ((K^\alpha)_{;\rho}),_\sigma),_\tau) - \frac{\partial \Gamma_{\rho\mu}^\alpha}{\partial B^\tau} \frac{\partial K^\mu}{\partial B^\sigma} - \frac{\partial \Gamma_{\sigma\mu}^\alpha}{\partial B^\tau} \frac{\partial K^\mu}{\partial B^\rho} \right. \\ &\quad \left. + \frac{\partial \Gamma_{\rho\sigma}^\mu}{\partial B^\tau} \frac{\partial K^\alpha}{\partial B^\mu} - \frac{\partial \Gamma_{\rho\mu}^\alpha}{\partial B^\sigma} \frac{\partial K^\mu}{\partial B^\tau} \right\}_{s_{\rho\sigma\tau}}, \end{aligned} \quad (4.2.52)$$

where $s_{\rho\sigma\tau}$ denotes the symmetrization

$$[a_{\rho\sigma\tau}]_{s_{\rho\sigma\tau}} = \frac{1}{6}(a_{\rho\sigma\tau} + a_{\rho\tau\sigma} + a_{\sigma\rho\tau} + a_{\sigma\tau\rho} + a_{\tau\rho\sigma} + a_{\tau\sigma\rho}). \quad (4.2.53)$$

In (4.2.51b) we carry out the total symmetrization with respect to all the four subscripts. This symmetrization is denoted by the subscript s. We obtain

$$F_{\rho\sigma\tau\pi} = \left[(((F_\rho)_{;\sigma}),_\tau),_\pi) + \frac{\partial \Gamma_{\rho\sigma}^\mu}{\partial B^\tau} F_{\mu\pi} + P_{(\rho\sigma\tau)} \frac{\partial \Gamma_{\rho\sigma}^\mu}{\partial B^\pi} F_{\mu\tau} \right]_s. \quad (4.2.54)$$

Switching over to the special geodesic coordinate system in which (4.2.46) is valid and considering the properties (4.2.49) of the curvature tensor, we have from (4.2.52, 54)

$$\frac{\partial^3 K^\alpha}{\partial B^\rho \partial B^\sigma \partial B^\tau} = \left[(((K^\alpha);_\rho);_\sigma);_\tau - R_{\rho\tau\mu}^\alpha \frac{\partial K^\mu}{\partial B^\sigma} \right]_{s_{\rho\sigma\tau}},$$

$$F_{\rho\sigma\tau} = [(((F_\rho);_\sigma);_\tau);_\pi]_s \quad \text{at } B = B^0. \quad (4.2.55)$$

Taking into consideration the last equations, it is easy to understand which covariant expression must be taken instead of (4.2.17d) in the arbitrary coordinate system. In order to obtain the covariant FDRs, we must make the substitution

$$l_{\alpha,\beta\gamma\delta} \rightarrow \{ [(((K^\alpha);_\rho);_\sigma);_\tau - R_{\rho\sigma\mu}^\alpha (K^\mu);_\tau - 3((K^\alpha);_\rho);_\mu r^{\mu\nu} ((F_\nu);_\sigma);_\tau]_{s_{\rho\sigma\tau}} \\ - (K^\alpha);_\mu r^{\mu\nu} [(((F_\nu);_\rho);_\sigma);_\tau - 3((F_\nu);_\rho);_\lambda r^{\lambda\pi} ((F_\pi);_\sigma);_\tau]_s \} \\ \times r^{\rho\beta} r^{\sigma\gamma} r^{\tau\delta} \quad \text{at } B = B^0. \quad (4.2.56)$$

Thus, the substitutions (4.2.36, 50, 56) and also the substitution $l_{\alpha\beta\gamma\delta} \rightarrow K^{\alpha\beta\gamma\delta}$ turn the precise cubic FDRs derived in Sect. 4.1.2 into the approximate covariant cubic FDRs. In doing so, of course, the matrix (4.1.26) should be written in the form $c^{\alpha\beta\gamma\delta}$. The ideology used in Sect. 4.2.4 provides the foundation of the rule for obtaining the covariant FDRs. We briefly remind the reader of this ideology. After substitution of the expressions (4.2.17) into the precise formulas, the FDRs become essentially different in the various curvilinear coordinate systems. They differ not only because one “looks at them in the various coordinate systems from different points of view”. From all different subvarieties of the relations we select the subvariety corresponding to the special geodesic coordinate system in which (4.2.46) is valid. Then we make an arbitrary curvilinear coordinate transformation, i.e. we begin “to look at the selected subvariety from different points of view”.

In conclusion we note that the curvature tensor is also helpful in writing in covariant form more precise two-subscript relations obtained by using (4.2.12).

4.3 Application of FDRs for Approximate Determination of the Coefficient Functions

4.3.1 Phenomenological Equation: Its Initial and Standard Forms

Let the nonequilibrium means $A_\alpha = \langle B_\alpha \rangle$ satisfy the phenomenological equations

$$\dot{A}_\alpha = \varphi_\alpha(A), \quad \alpha = 1, \dots, r. \quad (4.3.1)$$

The absence of the after-effect in (4.3.1) is in agreement with the assumption that the process $B(t)$ is a process without after-effect, i.e. a Markov process. Considering the form of the phenomenological equations and of the free energy $F(A)$, one can approximately determine the coefficients of the master equation. We will deal with this problem in this section.

It is convenient to suppose that the equilibrium values A_α^0 minimizing the free energy are equal to zero. This assumption is not a restriction of the generality since we can make the change of coordinates $A \rightarrow A - A_0$ if necessary. Then

$$\partial F(A)/\partial A_\alpha = 0 \quad \text{for } A = 0. \quad (4.3.2)$$

Since the equilibrium values are stable and, consequently, do not change in time, the right-hand side of (4.3.1) must satisfy the equation

$$\varphi_\alpha(0) = 0, \quad \alpha = 1, \dots, r. \quad (4.3.3)$$

It should be noted that (4.3.1) has macroscopic sense. Therefore the $\varphi_\alpha(A)$ cannot be regarded as functions determined with macroscopic accuracy; in other words, $\varphi_\alpha(A)$ are determined with an inaccuracy of $o(1)$ in the parameter k or kT . Hence, (4.3.1) can be interpreted both as $\langle \dot{B}_\alpha \rangle = \varphi_\alpha(\langle B \rangle)$ and as $\langle \dot{B}_\alpha \rangle = \langle \varphi_\alpha(B) \rangle$ with equal success. In spite of this inaccuracy, we additionally demand that the functions $\varphi_\alpha(A)$ satisfy (4.3.3) exactly.

Writing (3.1.76) for $m = 1$ gives

$$\langle \dot{B}_\alpha \rangle_x = \kappa_\alpha(x), \quad (4.3.4)$$

where

$$\langle \dots \rangle_x = \int \langle \dots \rangle_B w_x(B) dB.$$

Let us consider the two possible variants of the connection between (4.3.1) and (4.3.4) in detail. We may treat $\langle \dot{B}_\alpha \rangle_x$ in (4.3.4) as

$$\langle \langle \dot{B} \rangle_A \rangle_x = \langle \dot{A}(A) \rangle_x \quad (4.3.5)$$

(then $\langle \dot{B} \rangle = \langle \varphi_\alpha(A) \rangle_x = \int \varphi_\alpha(A) w_x(A) dA$) or as $\langle \dot{A}_\alpha \rangle_{A(x)}$. In the first case we have

$$\int \varphi_\alpha(A) w_x(A) dA = \kappa_\alpha(x) \quad (4.3.6)$$

and in the second case

$$\varphi_\alpha(A(x)) = \kappa_\alpha(x), \quad \varphi_\alpha(A) = \kappa_\alpha(x(A)). \quad (4.3.7)$$

Here the simplest dependence (3.1.38) is taken as the dependence $x(A)$. Then

$$\varphi_\alpha(x) = \kappa_\alpha(\partial F(A)/\partial A). \quad (4.3.8)$$

Either of the interpretations (4.3.6, 8) is admissible since the difference between (4.3.6) and (4.3.8) has the order of k and the function $\varphi_\alpha(A)$ is defined with an inaccuracy $o(1)$ in k as mentioned earlier. We choose the interpretation (4.3.8), i.e.

$$\dot{A}_\alpha = \kappa_\alpha(x(A)) \quad (4.3.9)$$

is referred to as the standard equation.

Taking into account that (4.2.6) is the inverse of the dependence $x_\alpha = \partial F(A)/\partial A_\alpha$, from (4.3.8) we get

$$\kappa_\alpha(x) = \varphi_\alpha(-\partial G(x)/\partial x). \quad (4.3.10)$$

Differentiating (4.3.10) with respect to $x_{\beta_1}, x_{\beta_2}, \dots$ and setting $x = 0$, we can find $l_{\alpha, \beta_1 \beta_2 \dots \beta_m}$ according to (4.1.6). Then using the Markov FDRs, one can express other matrices $l_{\alpha\beta}, l_{\alpha\beta_\gamma}, l_{\alpha\beta_\gamma}, l_{\alpha\beta_\gamma, \delta}$, etc., (four-subscript matrices only partially) in terms of $l_{\alpha, \beta_1 \beta_2 \dots \beta_m}$. Using the matrices just obtained and the formulas (4.2.8, 12) approximately relating the functions $K_{\alpha_1 \dots \alpha_n}(B)$ to $\kappa_{\alpha_1 \dots \alpha_n}(x)$, we can find the coefficient functions $K_{\alpha_1 \dots \alpha_n}(B)$ (some of them only partially) with any desired accuracy. Changing variables $B = -\partial G(x)/\partial x_\alpha$ in (4.2.8) yields

$$K_{\alpha_1 \dots \alpha_n}(B) = \kappa_{\alpha_1 \dots \alpha_n} \left(\frac{\partial F(B)}{\partial B} \right) [1 + \mathcal{O}(k)] . \quad (4.3.11)$$

After the same change of variables, (4.2.12) takes the form

$$\begin{aligned} \kappa_{\alpha_1 \dots \alpha_n} \left(\frac{\partial F(B)}{\partial B} \right) &= \left[K_{\alpha_1 \dots \alpha_n}(B) - \frac{1}{2} kT \frac{\partial K_{\alpha_1 \dots \alpha_n}}{\partial B_\beta} F_{\beta\rho}^{-1} F_{\rho\sigma\tau} F_{\sigma\tau}^{-1} \right. \\ &\quad \left. + \frac{1}{2} kT \frac{\partial^2 K_{\alpha_1 \dots \alpha_n}}{\partial B_\beta \partial B_\gamma} F_{\beta\gamma}^{-1} \right] [1 + \mathcal{O}(k^2)] . \end{aligned} \quad (4.3.12)$$

Here we have used the equation $G_{\delta\alpha} = -F_{\delta\alpha}^{-1}$ and (4.2.19a). Keeping the same degree of accuracy, one can substitute $\kappa_{\alpha_1 \dots \alpha_n}$ for $K_{\alpha_1 \dots \alpha_n}$ in the terms with the factor kT . Then we have

$$\begin{aligned} K_{\alpha_1 \dots \alpha_n}(B) &= \left[\kappa_{\alpha_1 \dots \alpha_n} \left(\frac{\partial F(B)}{\partial B} \right) + \frac{1}{2} kT \frac{\partial \kappa_{\alpha_1 \dots \alpha_n} (\partial F / \partial B)}{\partial x_\gamma} F_{\gamma\sigma\tau} F_{\sigma\tau}^{-1} \right. \\ &\quad \left. - \frac{1}{2} kT \frac{\partial^2 \kappa_{\alpha_1 \dots \alpha_n} (\partial F / \partial B)}{\partial B_\beta \partial B_\gamma} F_{\beta\gamma}^{-1} \right] [1 + \mathcal{O}(k^2)] . \end{aligned} \quad (4.3.13)$$

Here, in the term with the first derivative, we have taken into account that $\partial/\partial B_\beta = (\partial x_\gamma/\partial B_\beta) \partial/\partial x_\gamma = F_{\gamma\beta} \partial/\partial x_\gamma$. If we also use

$$\frac{\partial^2}{\partial B_\beta \partial B_\gamma} = F_{\sigma\beta} F_{\tau\gamma} \frac{\partial^2}{\partial x_\sigma \partial x_\tau} + F_{\sigma\beta\gamma} \frac{\partial}{\partial x_\sigma} , \quad (4.3.14)$$

we shall obtain

$$\begin{aligned} K_{\alpha_1 \dots \alpha_n}(B) &= \left[\kappa_{\alpha_1 \dots \alpha_n} \left(\frac{\partial F(B)}{\partial B} \right) - \frac{1}{2} kT \frac{\partial^2 \kappa_{\alpha_1 \dots \alpha_n}}{\partial x_\sigma \partial x_\tau} \left(\frac{\partial F}{\partial B} \right) F_{\sigma\tau} \right] \\ &\quad \times [1 + \mathcal{O}(k^2)] . \end{aligned} \quad (4.3.15)$$

One can regard (4.3.11, 15) as the inverse of (4.2.8, 12), respectively.

4.3.2 Linear Approximation

In this approximation the expansion of (4.3.10)

$$\varphi_\alpha(-\partial G(x)/\partial x) = l_{\alpha\beta} x_\beta + \frac{1}{2} l_{\alpha\beta\gamma} x_\beta x_\gamma + \dots \quad (4.3.16)$$

must contain only the terms that are linear in x . Then

$$\kappa_\alpha(x) = l_{\alpha\beta} x_\beta , \quad (4.3.17)$$

where

$$l_{\alpha,\beta} = \frac{\partial \varphi_\alpha}{\partial A_\gamma}(0) F_{\gamma\beta}^{-1}(0) = \frac{\partial \varphi_\alpha}{\partial A_\gamma}(0) \frac{\partial A_\gamma}{\partial x_\beta}(0). \quad (4.3.18)$$

Knowing $l_{\alpha,\beta}$ and using (4.1.11), we can obtain

$$l_{\alpha\beta} = -2kT g_{\alpha\beta}^+ l_{\alpha,\beta} \quad (2g_{\alpha\beta}^+ = 1 + \varepsilon_\alpha \varepsilon_\beta). \quad (4.3.19)$$

In the linear approximation $\kappa_{\alpha\beta}(x) = l_{\alpha\beta}$. Applying (4.3.11), from the last equation and (4.3.10, 17) we find

$$K_{\alpha\beta}(B) = -2kT g_{\alpha\beta}^+ l_{\alpha,\beta}, \quad (4.3.20a)$$

$$K_\alpha(B) = l_{\alpha,\beta} \frac{\partial F(B)}{\partial B_\beta}, \quad (4.3.20b)$$

where $l_{\alpha,\beta}$ is determined by (4.3.18). Consequently, in the given approximation the master equation assumes the form of the Fokker–Planck equation

$$\dot{w}(B) = -\frac{\partial}{\partial B_\alpha} \left[l_{\alpha,\beta} \frac{\partial F(B)}{\partial B_\beta} w(B) \right] + \frac{1}{2} kT g_{\alpha\beta}^+ l_{\alpha,\beta} \frac{\partial^2 w(B)}{\partial B_\alpha \partial B_\beta}. \quad (4.3.21)$$

The Langevin equation

$$\dot{B}_\alpha = l_{\alpha,\beta} \frac{\partial F(B)}{\partial B_\beta} + \xi_\alpha(t) \quad (4.3.22)$$

corresponds to this equation, where

$$\langle \xi_\alpha(t_1), \xi_\beta(t_2) \rangle = -2kT g_{\alpha\beta}^+ l_{\alpha,\beta} \delta(t_{12}). \quad (4.3.23)$$

In (4.3.21, 22) we can take $K_\alpha(B) = \varphi_\alpha(B)$ instead of $K_\alpha(B) = l_{\alpha,\beta} \partial F(B)/\partial B_\beta$ with equal success. However, if the functions $\varphi_\alpha(B)$ are unknown, it is reasonable to use equations (4.3.21, 22) containing the unknown matrix $l_{\alpha,\beta}$ which is a simpler object than the functions $\varphi_\alpha(B)$.

As we have already pointed out in Sect. 1.2.1, determination of the diffusion coefficient $K_{\alpha\beta}$ and of the complete operator of the Fokker–Planck equation was first made by Einstein [4.3] in 1905 in his work concerning Brownian motion. In his particular simple case the functions $\varphi_\alpha(A)$ were linear, and the energy replacing the free energy was quadratic. The formulas obtained above are valid, of course, not just for quadratic function $F(B)$.

4.3.3 Linear–Quadratic Approximation

If we consider more precisely the expansion (4.3.16), according to which $l_{\alpha,\beta_1 \dots \beta_s}$ are expressed in terms of $\varphi_\alpha(A)$, we should retain both the linear and quadratic terms. If $l_{\alpha,\beta\gamma}$ is known, then using (4.1.16, 18) one can find $l_{\alpha\beta,\gamma}$ and $l_{\alpha\beta\gamma}$ and, therefore, the functions

$$\kappa_{\alpha\beta}(x) = l_{\alpha\beta} + l_{\alpha\beta,\gamma} x_\gamma, \quad \kappa_{\alpha\beta\gamma}(x) = l_{\alpha\beta\gamma}, \quad (4.3.24)$$

corresponding to our approximation.

Then, applying (4.3.11) we can determine

$$\begin{aligned} K_{\alpha\beta}(B) &= l_{\alpha\beta} + l_{\alpha\beta,\gamma} \frac{\partial F(B)}{\partial B_\gamma} \\ &= -2kT \vartheta_{\alpha\beta}^+ l_{\alpha,\beta} + kT(\varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma l_{\gamma,\alpha\beta} - l_{\alpha,\beta\gamma} - l_{\beta,\alpha\gamma}) \frac{\partial F(B)}{\partial B_\gamma}, \end{aligned} \quad (4.3.25)$$

$$K_{\alpha\beta\gamma}(B) = 2(kT)^2 \vartheta_{\alpha\beta\gamma}^- (l_{\alpha,\beta\gamma} + l_{\beta,\alpha\gamma} + l_{\gamma,\alpha\beta}), \quad (4.3.26)$$

where

$$2\vartheta_{\alpha\beta\gamma}^- = 1 - \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma. \quad (4.3.27)$$

However, it should be noted that the simple formula

$$K_\alpha(B) = l_{\alpha,\beta} \frac{\partial F(B)}{\partial B_\beta} + \frac{1}{2} l_{\alpha,\beta\gamma} \frac{\partial B(B)}{\partial B_\beta} \frac{\partial F(B)}{\partial B_\gamma} \quad (4.3.28)$$

obtained by virtue of (4.3.9, 11) from

$$\kappa_\alpha(x) = l_{\alpha,\beta} x_\beta + \frac{1}{2} l_{\alpha,\beta\gamma} x_\beta x_\gamma \quad (4.3.29)$$

is insufficient in the linear-quadratic approximation. If (4.3.28) is used, the solution of the stationary master equation will differ from the initial probability density

$$w_{\text{eq}}(B) = \text{const} \cdot \exp[-F(B)/kT]. \quad (4.3.30)$$

This discrepancy is inadmissible. As is shown in Appendix 5, the functions $K_\alpha(B)$ should be determined with better accuracy in the linear-quadratic approximation than in the linear one. Now, the accuracy of determination of $K_\alpha(B)$ must be greater than the accuracy of determination of functions (4.3.25, 26). The error of determination of $K_\alpha(B)$ must be $\mathcal{O}(k^{3/2})$, and not $\mathcal{O}(k)$. Therefore, one should take (4.3.15) and not (4.3.11). According to (4.3.15), from (4.3.29) we obtain

$$K_\alpha(B) = l_{\alpha,\beta} \frac{\partial F(B)}{\partial B_\beta} + \frac{1}{2} l_{\alpha,\beta\gamma} \frac{\partial F(B)}{\partial B_\beta} \frac{\partial F(B)}{\partial B_\gamma} - \frac{1}{2} kT_{\alpha,\beta\gamma} F_{\beta\gamma}(B). \quad (4.3.31)$$

The first two terms on the right-hand side of (4.3.31) vanish at $B = 0$ according to (4.3.2); the last term is not required to have this property. Therefore, it follows from (4.3.31) that, generally speaking, $K_\alpha(0) \neq 0$. The last term in (4.3.31) causes a small shift of the characteristic $I_\alpha = K_\alpha(B)$ in the vertical direction. This has been discussed in Sect. 3.3.3. The term with kT in (4.3.31) is necessary to avoid the detection of fluctuations and to preserve the validity of the equation $\varphi_\alpha(0) = 0$, i.e. of (4.1.10).

If instead of (4.3.29) we substitute (4.3.10) into (4.3.15), we arrive at

$$K_\alpha(B) = \varphi_\alpha(B) + \frac{kT}{2} \frac{\partial \varphi_\alpha(B)}{\partial B_\beta} F_{\beta\gamma}^{-1}(B) F_{\gamma\delta\varepsilon} F_{\delta\varepsilon}^{-1} - \frac{kT}{2} \frac{\partial^2 \varphi_\alpha(B)}{\partial B_\beta \partial B_\sigma} F_{\rho\sigma}^{-1}(B). \quad (4.3.32)$$

In the linear-quadratic approximation both (4.3.31, 32) can be applied with equal success.

4.3.4 Linear–Quadratic–Cubic Approximation

In this approximation one should retain the linear, quadratic and cubic terms in (4.3.16). Therefore, we have

$$\kappa_\alpha(x) = l_{\alpha,\beta}x_\beta + \frac{1}{2}l_{\alpha,\beta\gamma}x_\beta x_\gamma + \frac{1}{6}l_{\alpha,\beta\gamma\delta}x_\beta x_\gamma x_\delta . \quad (4.3.33)$$

The other functions are taken as

$$\kappa_{\alpha\beta}(x) = l_{\alpha\beta} + l_{\alpha\beta,\gamma}x_\gamma + \frac{1}{2}l_{\alpha\beta,\gamma\delta}x_\gamma x_\delta , \quad (4.3.34a)$$

$$\kappa_{\alpha\beta\gamma}(x) = l_{\alpha\beta\gamma} + l_{\alpha\beta\gamma,\delta}x_\delta , \quad (4.3.34b)$$

$$\kappa_{\alpha\beta\gamma\delta}(x) = l_{\alpha\beta\gamma\delta} . \quad (4.3.34c)$$

When the matrix $l_{\alpha,\beta\gamma\delta}$ in (4.3.33) is known and the dissipationally undeterminable matrix $c_{\alpha\beta,\gamma\delta}$ satisfying the condition (4.1.27) is specified, we can determine the matrices $l_{\alpha\beta,\gamma\delta}, l_{\alpha\beta\gamma,\delta}, l_{\alpha\beta\gamma\delta}$ according to (4.1.28, 29, 31). Thus, the functions (4.3.34) are also determined (two- and three-subscript matrices in (4.3.34) have been determined earlier). Now, applying the simple formula (4.3.11), we find

$$\begin{aligned} K_{\alpha\beta\gamma}(B) &= l_{\alpha\beta\gamma} + l_{\alpha\beta\gamma,\delta}\partial F(B)/\partial B_\delta , \\ K_{\alpha\beta\gamma\delta}(B) &= l_{\alpha\beta\gamma\delta} . \end{aligned} \quad (4.3.35)$$

The relative error of these equations is $\mathcal{O}(k)$, and according to the consideration given in Appendix 5, it is admissible. As one can see from (A5.16), the functions $K_\alpha(B)$ and $K_{\alpha\beta}(B)$ should be determined with more accuracy, namely, by using (4.3.15). If the total function (4.3.10) is substituted into (4.3.15), one can use (4.3.32) in the linear–quadratic–cubic approximation as well. If, in contrast, (4.3.33) is used, we shall obtain

$$\begin{aligned} K_\alpha(B) &= l_{\alpha,\beta}\frac{\partial F}{\partial B_\beta} + \frac{1}{2}l_{\alpha,\beta\gamma}\frac{\partial F}{\partial B_\beta}\frac{\partial F}{\partial B_\gamma} + \frac{1}{6}l_{\alpha,\beta\gamma\delta}\frac{\partial F}{\partial B_\beta}\frac{\partial F}{\partial B_\gamma}\frac{\partial F}{\partial B_\delta} \\ &\quad - \frac{1}{2}kT\left(l_{\alpha,\gamma\delta} + l_{\alpha,\beta\gamma\delta}\frac{\partial F}{\partial B_\beta}\right)F_{\gamma\delta}(B) . \end{aligned} \quad (4.3.36)$$

Any of the formulas (4.3.32, 36) is admissible in the approximation being considered. Finally, applying (4.3.15) to (4.3.34a), we find the last unknown function

$$K_{\alpha\beta}(B) = l_{\alpha\beta} + l_{\alpha\beta,\gamma}\frac{\partial F(B)}{\partial B_\gamma} + \frac{1}{2}l_{\alpha\beta,\gamma\delta}\frac{\partial F(B)}{\partial B_\gamma}\frac{\partial F(B)}{\partial B_\delta} - \frac{1}{2}kTl_{\alpha\beta,\gamma\delta}\frac{\partial^2 F(B)}{\partial B_\gamma\partial B_\delta} . \quad (4.3.37)$$

Other functions $K_{\alpha_1\dots\alpha_n}, n > 4$ are set equal to zero. No more approximations will be considered here.

In conclusion, we note that the formulas determining the master equation coefficient functions become invalid in the anomalous cases when the functions $\varphi_\alpha(A)$ are undifferentiable at $A = 0$. Then (4.3.10) cannot be used since in doing so $\kappa_\alpha(x)$ will be undifferentiable. In this case $\kappa_\alpha(x)$ should be determined according to (4.3.6) or (3.1.42) at $K_\alpha(B) = \varphi_\alpha(B) + \text{const}$ ($\text{const} \sim k$). An example of the anomalous case will be given in Sect. 4.4.5.

4.3.5 Some Formulas of the Modified Version

The above considerations can also be carried out in the modified version. Of course, one should use here (4.1.33), etc. In the modified version all formulas should have a form analogous to the form of the unmodified ones. The important difference is that $k, L_{\dots}, -S(B)$ are substituted for $kT, l_{\dots}, F(B)$, respectively. Thus, instead of (4.3.20) we have

$$\begin{aligned} K_\alpha(B) &= -L_{\alpha,\beta} \frac{\partial S(B)}{\partial B_\beta}, \\ K_{\alpha\beta}(B) &= -2k g_{\alpha\beta}^+ L_{\alpha,\beta} \end{aligned} \quad (4.3.38)$$

and instead of (4.3.25, 26), we have

$$\begin{aligned} K_{\alpha\beta\gamma}(B) &= L_{\alpha\beta\gamma}, \\ K_{\alpha\beta}(B) &= L_{\alpha\beta} - L_{\alpha\beta,\gamma} \frac{\partial S(B)}{\partial B_\gamma}, \end{aligned} \quad (4.3.39)$$

where $L_{\alpha\beta\gamma}$ and $L_{\alpha\beta,\gamma}$ are determined by (4.1.33). The analogue of (4.3.31) will be of the form

$$K_\alpha(B) = -L_{\alpha,\beta} \frac{\partial S(B)}{\partial B_\beta} + \frac{1}{2} L_{\alpha,\beta\gamma} \frac{\partial S(B)}{\partial B_\beta} \frac{\partial S(B)}{\partial B_\gamma} + \frac{1}{2} k L_{\alpha,\beta\gamma} \frac{\partial^2 S(B)}{\partial B_\beta \partial B_\gamma}. \quad (4.3.40)$$

The phenomenological equation

$$\dot{A}_\alpha = -L_{\alpha,\beta} \frac{\partial S(A)}{\partial A_\beta} + \frac{1}{2} L_{\alpha,\beta\gamma} \frac{\partial S(A)}{\partial A_\beta} \frac{\partial S(A)}{\partial A_\gamma} \quad (4.3.41)$$

corresponds to (4.3.40). There is no need to give the other formulas in the modified version.

4.3.6 Remark About the Use of Covariant FDRs for Constructing Coefficient Functions

The covariant FDRs considered in Sects. 4.2.3–5 can be used for constructing the coefficient functions and the Markov operator on the basis of the phenomenological relaxation equation if $B = (B^\alpha)$ are the curvilinear coordinates of a certain space with metric tensor $g_{\alpha\beta}$.

We take as an example the problem of finding $K_{\alpha\beta}(B)$ in the linear–quadratic approximation. Since

$$(K^{\alpha\beta})_{;\rho} = \frac{\partial K^{\alpha\beta}}{\partial B^\rho} + \Gamma_{\rho\nu}^\alpha K^{\nu\beta} + \Gamma_{\rho\nu}^\beta K^{\nu\alpha}, \quad (4.3.42)$$

the equation

$$K^{\alpha\beta}(B) = K^{\alpha\beta}(B_0) + \left(\frac{\partial K_{\alpha\beta}}{\partial B^\rho} \right)_0 (B^\rho - B^{0\rho}) \quad (4.3.43)$$

can be written in the equivalent form

$$K^{\alpha\beta}(B) = (K^{\alpha\beta})_0 + [(K^{\alpha\beta})_{;\rho} - \Gamma_{\rho\nu}^\alpha K^{\nu\beta} - \Gamma_{\rho\nu}^\beta K^{\nu\alpha}]_0 (B^\rho - B^{0\rho}). \quad (4.3.44)$$

The derivative $[(K^{\alpha\beta})_{;\rho}]_0$ in (4.3.44) is expressed in terms of $K^\alpha(B)$ according to the relation (4.1.16), into which we should make the substitution of (4.2.33). The matrix $(K^{\alpha\beta})_0$ on the right-hand side of (4.3.44) is determined by (4.2.24a).

4.4 Examples of the Application of Linear Nonequilibrium Thermodynamics Relations

4.4.1 Twofold Correlators in the Case of a System with Linear Relaxation and Quadratic Free Energy

Before considering specific examples, we derive several general formulas. For the system with linear relaxation the phenomenological equations (4.3.1) assume the form (3.1.18). Passing from the mean values of internal parameters to random values B_α , we obtain from (3.1.18)

$$\dot{B}_\alpha = -d_{\alpha\beta} B_\beta + \xi_\beta, \quad \beta = 1, 2, \dots. \quad (4.4.1)$$

Here ξ_1, \dots, ξ_r are random processes with zero mean and with the correlation function (4.3.23). Equation (4.4.1) coincides with (4.3.22) for quadratic free energy (3.1.19) if the equation

$$d_{\alpha\gamma} = -l_{\alpha,\beta} u_{\beta\gamma} \quad (4.4.2)$$

is valid.

Let us write down (4.4.1) in matrix form:

$$\dot{B}(t) = -\hat{D}B(t) + \xi(t), \quad (4.4.3)$$

where

$$\hat{D} = \|d_{\alpha\beta}\|, \quad B = \begin{vmatrix} B_1 \\ \vdots \\ B_r \end{vmatrix}, \quad \xi = \begin{vmatrix} \xi_1 \\ \vdots \\ \xi_r \end{vmatrix}. \quad (4.4.4)$$

In matrix form (4.4.2) and (4.3.23) will be of the form

$$\hat{D} = -\hat{L}\hat{U}, \quad (4.4.5)$$

$$\langle \xi(t_1)\xi^T(t_2) \rangle = -2kT\hat{L}^0\delta(t_1 - t_2), \quad (4.4.6)$$

where

$$\hat{L} = \|l_{\alpha,\beta}\|, \quad \hat{L}^0 = \|g_{\alpha\beta}^+ l_{\alpha,\beta}\|, \quad \hat{U} = \|u_{\alpha\beta}\|, \quad \xi^T = \|\xi_1, \dots, \xi_r\|. \quad (4.4.7)$$

Passing over to the spectra

$$\begin{aligned} B_\alpha(\omega) &= (2\pi)^{-1/2} \int \exp(-i\omega t) B_\alpha(t) dt, \\ \xi_\alpha(\omega) &= (2\pi)^{-1/2} \int \exp(-i\omega t) \xi_\alpha(t) dt, \end{aligned} \quad (4.4.8)$$

we can write (4.4.1) as

$$(i\omega \hat{I} + \hat{D})B(\omega) = \xi(\omega) \quad (\hat{I} = \|\delta_{\alpha\beta}\|). \quad (4.4.9)$$

Solving this equation for $B(\omega)$ yields

$$B(\omega) = (i\omega \hat{I} + \hat{D})^{-1} \xi(\omega). \quad (4.4.10)$$

From (4.4.10) it follows directly that

$$\langle B(\omega_1), B^T(\omega_2) \rangle = (i\omega_1 \hat{I} + \hat{D})^{-1} \langle \xi(\omega_1), \xi^T(\omega_2) \rangle (i\omega_2 \hat{I} + \hat{D}^T)^{-1}. \quad (4.4.11)$$

Using formula (A6.2), which establishes the relationship between the correlator of the spectra and the spectral density, we obtain from (4.4.11)

$$\hat{S}_B(\omega) = (i\omega \hat{I} + \hat{D})^{-1} \hat{S}_\xi(\omega) (-i\omega \hat{I} + \hat{D}^T)^{-1} \quad (\hat{S}(\omega) = \|S_{\alpha\beta}(\omega)\|). \quad (4.4.12)$$

By virtue of (4.4.6) and (A6.5) we have

$$\hat{S}_\xi(\omega) = -2kT\hat{L}^0. \quad (4.4.13)$$

Therefore, from (4.4.12) we get

$$\hat{S}_B(\omega) = -2kT(i\omega \hat{I} + \hat{D})^{-1} \hat{L}^0 (-i\omega \hat{I} + \hat{D}^T)^{-1}. \quad (4.4.14)$$

As a consequence of (4.1.12), the matrix $\hat{L}^0 = \|\vartheta_{\alpha\beta}^+ l_{\alpha,\beta}\|$ can be represented in the form $(\hat{L} + \hat{L}^T)/2$.

In the particular case where all the parameters have the same time-evenness, the matrix L is symmetrical by virtue of (4.1.13), so that (4.4.14) can be reduced to the form

$$\hat{S}_B(\omega) \equiv -2kT(\omega^2 \hat{I} + \hat{D}^2)^{-1} \hat{L}. \quad (4.4.15)$$

One can verify this by applying the equations

$$\hat{L}(-i\omega \hat{I} + \hat{D}^T)^{-1} = \hat{L}(-i\omega \hat{I} - \hat{U}\hat{L})^{-1} = (-i\omega \hat{I} - \hat{L}\hat{U})^{-1} \hat{L}, \quad (4.4.16)$$

where (4.4.5) is used.

Equation (4.4.3) can be also used in the time representation. From this equation we easily derive

$$\frac{d}{dt} \langle B(t), B^T(t_1) \rangle = -\hat{D} \langle B(t), B^T(t_1) \rangle \quad \text{for } t > t_1. \quad (4.4.17)$$

Solving this equation subject to the initial condition

$$\langle B(t_1), B^T(t_1) \rangle = kT\hat{U}^{-1}, \quad (4.4.18)$$

which follows from the stationary probability density

$$w(B) = \text{const} \cdot \exp(-F(B)/kT) = \text{const} \cdot \exp\left(-\frac{1}{2kT} u_{\alpha\beta} B_\alpha B_\beta\right), \quad (4.4.19)$$

where

$$u_{\alpha\beta} = \partial^2 F(B)/\partial B_\alpha \partial B_\beta = \partial x_\alpha(B)/\partial B_\beta \quad (4.4.20)$$

with free energy (3.1.19), we get

$$\langle B(t_2), B^T(t_1) \rangle = kT \exp(-\hat{D}t_{21}) \hat{U}^{-1}, \quad \text{for } t_2 \geq t_1 \quad (t_{21} = t_2 - t_1). \quad (4.4.21)$$

To avoid the necessity of calculating $\exp(-\hat{D}t_{21})$, one can solve (4.4.17) by the Laplace transformation method. For the Laplace transform

$$\hat{F}(p) = \int_0^\infty \exp(-pt) \hat{R}(t) dt \quad (4.4.22)$$

of the matrix correlator $\hat{R}(t) = \langle B(t), B^T(0) \rangle$ we easily obtain

$$\hat{F}(p) = (p\hat{I} + \hat{D})^{-1} \hat{R}(0) = kT(p\hat{I} + \hat{D})^{-1} \hat{U}^{-1}. \quad (4.4.23)$$

After the inversion of the matrix $p\hat{I} + \hat{D}$, the matrix $\hat{R}(t)$ can be found by using tables of Laplace transforms or with the help of operational calculus tables [the Carson–Laplace transform of $\hat{R}(t)$ is equal to $p\hat{F}(p)$]. Using $\hat{F}(p)$, the matrix spectral density of the fluctuations $B(t)$ can be written as

$$S_{\alpha\beta}(\omega) = F_{\alpha\beta}(i\omega) + F_{\beta\alpha}(-i\omega), \quad (4.4.24)$$

i.e. by virtue of (4.4.23)

$$\hat{S}_B(\omega) = kT[(i\omega\hat{I} + \hat{D})^{-1} \hat{U}^{-1} + \hat{U}^{-1}(-i\omega\hat{I} + \hat{D}^T)^{-1}], \quad (4.4.25)$$

which is equivalent to (4.4.14).

We now leave the general formulas and proceed to particular examples.

4.4.2 Example: Electrokinetic Phenomena

Suppose we have two vessels containing gas and connected by a porous partition. In the first vessel the number of moles of the gas is equal to C_1 , and in the second vessel this number is equal to C_2 . The vessels have identical temperatures. The gas can flow through the partition from one vessel to the other, and the total number of moles $C = C_1 + C_2$ remains unchanged. The gas in each vessel is characterized by its own pressure and electrical potential. Let $u = q/C_0$ be the potential difference across the vessels, and C_0 be the corresponding capacitance. As is well known, the electrostatic energy is equal to $q^2/(2C_0)$. Let us denote the free energy of the gas in the first vessel by $F_1(T, C_1)$ and the free energy of the gas in the second vessel by $F_2(T, C_2) = F_2(T, C - C_1)$. If we also take into account the electrostatic energy, the total free energy is equal to

$$F(q, C_1) = F_1(T, C_1) + F_2(T, C - C_1) + \frac{1}{2} C_0^{-1} q^2. \quad (4.4.26)$$

We regard q and C_1 as the internal parameters B_1 and B_2 . Using (4.4.26), according to (3.1.38), we find the parameters conjugate to q and C_1 :

$$x_1 = \partial F / \partial q = q/C_0 = u , \quad (4.4.27a)$$

$$x_2 = \partial F / \partial C_1 = \mu^{(1)}(T, C_1) - \mu^{(2)}(T, C - C_1) . \quad (4.4.27b)$$

Here we have used the formulas

$$\begin{aligned} \mu^{(1)}(T, C_1) &= \partial F_1(T, C_1) / \partial C_1 , \\ \mu^{(2)}(T, C_2) &= \partial F_2(T, C_2) / \partial C_2 , \end{aligned} \quad (4.4.28)$$

which are analogous to (3.4.13). By virtue of (3.4.22), we find from (4.4.27)

$$x_2 = \partial F / \partial C_1 = RT [\ln(C_1/V_1) - \ln((C - C_1)/V_2)] . \quad (4.4.29)$$

Considering the ideal gas equation $C_i RT = p_i V_i$ gives

$$x_2 = RT(\ln p_1 - \ln p_2) . \quad (4.4.30)$$

For small pressure differences one can use the approximate equation

$$x_2 = v \Delta p , \quad (4.4.31)$$

where $\Delta p = p_1 - p_2$ and $v = RT/p_1$ is the molar volume.

For the case considered we write the relaxation equations

$$\dot{A}_\alpha = l_{\alpha, \beta} \frac{\partial F(A)}{\partial A_\beta} \equiv l_{\alpha, \beta} x_\beta(A) , \quad (4.4.32)$$

which are obtained by averaging (4.3.22). In the present case, by virtue of (4.4.27a, 31) these relaxation equations assume the form

$$\begin{aligned} \dot{q} &= l_{1,1} x_1 + l_{1,2} x_2 = l_{1,1} u + l_{1,2} v \Delta p , \\ \dot{C}_1 &= l_{2,1} x_1 + l_{2,2} x_2 = l_{2,1} u + l_{2,2} v \Delta p . \end{aligned} \quad (4.4.33)$$

Both q and C_1 are time-even. For this reason the Onsager relation

$$l_{1,2} = l_{2,1} \quad (4.4.34)$$

must be fulfilled. Applying the formulas from the previous section, we can find the correlator of the random processes $C_1(t)$, $q(t)$ [or $u(t)$]. When $l_{2,1} = l_{1,2} = 0$ and $V_1 = V_2$, we obtain from (4.4.29, 33)

$$\dot{A} = -2lRT \langle C_1 \rangle^{-1} \Delta , \quad (4.4.35)$$

where

$$\Delta = C_1 - C/2, \quad l = -l_{2,2} . \quad (4.4.36)$$

Taking into account that by virtue of (4.4.20, 29)

$$u_{22} = \partial x_2 / \partial C_1 = 2RT / \langle C_1 \rangle = 4RT/C , \quad (4.4.37)$$

and using (4.4.21), we obtain

$$\langle C_1(t), C_1(0) \rangle = (kT/u_{22}) \exp(-d_{22}t) = [C/(4N_A)] \exp(-d_{22}t), \quad (4.4.38)$$

where $d_{22} = 4lRT/C$ and N_A is Avogadro's number.

4.4.3 Thermokinetic Processes

Let the potential difference across the above-mentioned vessels containing gas be equal to zero, but let them have different temperatures so that there exists a heat exchange between them. For each vessel, (3.4.14) can be written as

$$dF_i = -S_i dT_i + \mu^{(i)} dC_i, \quad i = 1, 2. \quad (4.4.39)$$

Introducing the internal energies $U_i = F_i + S_i T_i$ of the gases in the vessels, we have $dU_i = T_i dS_i + \mu^{(i)} dC_i$, i.e.

$$\begin{aligned} dS_1 &= T_1^{-1} dU_1 - T_1^{-1} \mu^{(1)} dC_1, \\ dS_2 &= T_2^{-1} dU_2 - T_2^{-1} \mu^{(2)} dC_2. \end{aligned} \quad (4.4.40)$$

When there is a heat exchange and an exchange of molecules, both the total energy $U_1 + U_2 = U$ and the total amount of gas $C_1 + C_2 = C$ remain unchanged. The total entropy is equal to the sum

$$S(U_1, C_1) = S_1(U_1, C_1) + S_2(U - U_1, C - C_1). \quad (4.4.41)$$

Considering (4.4.40), we find its increment

$$dS = (T_1^{-1} - T_2^{-1}) dU_1 - (T_1^{-1} \mu^{(1)} - T_2^{-1} \mu^{(2)}) dC_1. \quad (4.4.42)$$

We will treat U_1 and C_1 as internal thermodynamic parameters. It is now convenient to determine the thermodynamic forces, i.e. the parameters conjugate to U_1 and C_1 according to (3.1.58). By virtue of (4.4.42) we have

$$X_1 = -\frac{\partial S(U_1, C_1)}{\partial U_1} = T_2^{-1} - T_1^{-1}, \quad (4.4.43a)$$

$$X_2 = -\frac{\partial S(U_1, C_1)}{\partial C_1} = T_1^{-1} \mu^{(1)} - T_2^{-1} \mu^{(2)}. \quad (4.4.43b)$$

If the volumes of the vessels are equal, by virtue of (3.4.22) we can write (4.4.43b) as

$$X_2 = R(\ln C_1 - \ln C_2) \quad (4.4.44)$$

(the terms with ζ_1 are not considered).

When the differences $T_1 - T_2 \equiv \Delta T$, $C_1 - C_2 = 2C_1 - C \equiv \Delta C$ are small, (4.4.43, 44) give

$$\begin{aligned} X_1 &= \Delta T/T^2, \\ X_2 &= R \Delta C/C_1. \end{aligned} \quad (4.4.45)$$

Let us write the modification of (4.4.32) for the process under study. By virtue of

(4.4.44) we arrive at

$$\begin{aligned}\dot{U}_1 &= L_{1,1}X_1 + L_{1,2}X_2 = L_{1,1}\Delta T/T^2 + L_{1,2}R\Delta C/C_1, \\ \dot{C}_1 &= L_{2,1}X_1 + L_{2,2}X_2 = L_{2,1}\Delta T/T^2 + L_{2,2}R\Delta C/C_1.\end{aligned}\quad (4.4.46)$$

As a consequence of the time-evenness of the parameters C_1 and U_1 , the Onsager relation

$$L_{1,2} = L_{2,1} \quad (4.4.47)$$

following from (4.1.33b) must be satisfied.

4.4.4 Thermoelectric Phenomena

Let there be two separate junctions of two different metals A and B and let them be placed into vessels with different temperatures. These junctions and a capacitor with capacitance C_0 are connected in series (Fig. 4.1). There is a charge q on the capacitor and a potential difference $u = q/C_0$ across it. For each vessel

$$dU_i = T_i dS_i, \quad i = 1, 2 \quad (4.4.48)$$

(see (2.2.18) taken at $r = 0$), where U_i and S_i are the internal energies and the vessel entropies, respectively. Summing the entropy variations $dS_i = dU_i/T_i$, we find the total entropy variation

$$dS = T_1^{-1} dU_1 + T_2^{-1} dU_2. \quad (4.4.49)$$

The energy variations dU_i are induced by the heat exchange between the vessels and by Joule heating produced in the resistors by the current flow. In this case the law of energy conservation takes the form

$$dU_1 + dU_2 + dU_C = 0, \quad (4.4.50)$$

where $U_C = q^2/2C_0$ is the electrical energy of the capacitor. It is assumed that the system is energetically isolated from external bodies. The resistance of the conductors outside the vessels is assumed negligible. Substituting $dU_2 = -dU_1 - (q/C_0)dq$ into (4.4.50) yields

$$dS = (T_1^{-1} - T_2^{-1})dU_1 - T_2^{-1}u dq, \quad (4.4.51)$$

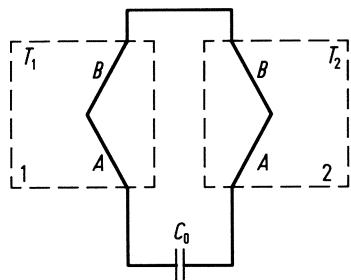


Fig. 4.1. Circuit with a capacitor and two junctions for illustrating the thermoelectric effect

where $u = q/C_0$. Using (4.4.51) and (3.1.58), we find that the thermodynamic forces

$$\begin{aligned} X_1 &= -\frac{\partial S(U_1, q)}{\partial U_1} = T_2^{-1} - T_1^{-1} \approx T^{-2} \Delta T, \\ X_2 &= -\frac{\partial S(U_1, q)}{\partial q} = \frac{u}{T_2} \approx \frac{u}{T} \end{aligned} \quad (4.4.52)$$

are the conjugates of the internal parameters U_1 and q . Here $\Delta T = T_1 - T_2$, $T \sim T_1, T_2$. The relaxation equations (4.4.32) are now of the form

$$\dot{U}_1 = L_{1,1}X_1 + L_{1,2}X_2 = L_{1,1}T^{-2}\Delta T + L_{1,2}T^{-1}u, \quad (4.4.53a)$$

$$\dot{q} \equiv I = L_{2,1}X_1 + L_{2,2}X_2 = L_{2,1}T^{-2}\Delta T + L_{2,2}T^{-1}u \quad (4.4.53b)$$

(I is the electric current). Here the Onsager relation $L_{1,2} = L_{2,1}$ must be satisfied.

The validity of the Onsager relations can be verified experimentally. Let us show how this can be done. First of all, for $\Delta T \neq 0$ we select the voltage u such that the current $I = \dot{q}$ controlled by an additional device is absent in the circuit. Then, from (4.4.53b) we obtain

$$L_{2,1} = -L_{2,2}T(u/\Delta T)_{I=0}. \quad (4.4.54)$$

The current I is equal to zero because in the case of different temperatures of the junctions a counteracting potential difference arises across the circuit; this potential difference is called the thermoelectric potential. Its magnitude is characterized by $(u/\Delta T)_{I=0}$. This expression appears in (4.4.54).

Furthermore, at a given nonzero value of the current I we choose the temperature difference such that U_1 (i.e. T_1) remains unchanged in time. From (4.4.53a) we will have

$$L_{1,2} = -L_{1,1}(\Delta T/(Tu))_{T_1=\text{const}}. \quad (4.4.55)$$

The temperature constancy that exists in spite of the presence of heat exchange can be explained by the fact that thermal energy is emitted at one junction and absorbed at the other when the current flows. This phenomenon is called the Peltier effect. It compensates the heat exchange due to heat conduction for $\Delta T \neq 0$. Owing to the Onsager relation $L_{1,2} = L_{2,1}$, the expressions (4.4.54, 55) related to the different effects must coincide. Thus, the magnitudes of these two effects are related.

4.4.5 Anomalous Case: Circuit with Ideal Detector

The case for which the precise formula

$$\kappa_\alpha(x) = \int K_\alpha(B) w_x(B) dB \quad (4.4.56)$$

[see (3.1.42)], cannot be replaced by the approximate formula

$$\kappa_\alpha(x) = K_\alpha(B(x)) \quad (4.4.57)$$

(where the dependence $B(x)$ is the inverse of the dependence $x_\alpha = \partial F(B)/\partial B_\alpha$), or even the more precise formula (4.2.12), is called the anomalous case. For example, let us consider an RC-circuit (Fig. 4.2) where the resistor is nonlinear, namely, it has unidirectional conduction. Its voltage-current characteristic has the form

$$I = f(V) = \begin{cases} SV & \text{for } V > 0, \\ 0 & \text{for } V < 0. \end{cases} \quad (4.4.58)$$

It is shown in Fig. 4.3. This circuit is described by the phenomenological equation

$$\dot{Q} = -f(Q/C), \quad (4.4.59)$$

where Q is the charge on the capacitor. This charge plays the role of the only internal parameter B_1 . The energy of the capacitor is equal to $W = Q^2/(2C)$, so that the equilibrium probability density of the charge assumes the form

$$w(Q) = \text{const} \cdot \exp(-\frac{1}{2}\beta C^{-1}Q^2) = (2\pi kTC)^{-1/2} \exp(-\frac{1}{2}\beta C^{-1}Q^2). \quad (4.4.60)$$

According to (3.1.29), we find the auxiliary nonequilibrium probability density to be

$$w_x(Q) = (2\pi kTC)^{-1/2} \exp[-\frac{1}{2}\beta C^{-1}(Q - Cx)^2]. \quad (4.4.61)$$

The force x has the meaning of an additional potential difference across the capacitor. By virtue of (4.4.61) equation (4.4.56) takes the form

$$\kappa_1(x) = \int K_1(Q)(2\pi kTC)^{-1/2} \exp[-\frac{1}{2}\beta C^{-1}(Q - Cx)^2] dQ. \quad (4.4.62)$$

How does one treat the right-hand side of (4.4.59) when fluctuations are taken into

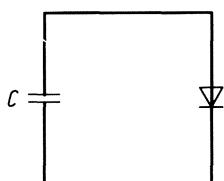


Fig. 4.2. Simple circuit with ideal detector

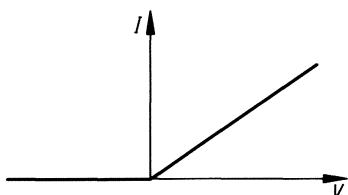


Fig. 4.3. Current-voltage characteristic of the ideal detector

account? Should one treat $-f(Q/C)$ as $K_1(Q)$ or as $\kappa_1(x(Q))$? In the latter case we have

$$\kappa_1(x) = -f(x) = \begin{cases} -Sx & \text{for } x > 0, \\ 0 & \text{for } x < 0 \end{cases} \quad (4.4.63)$$

since $x(Q) = dW/dQ = Q/C$. It is easy to appreciate that the treatment (4.4.63) is erroneous since according to (4.4.62) the derivative of the function $\kappa_1(x)$ must be continuous, but the derivative of (4.4.61) has a jump discontinuity. Instead of (4.4.63) let us try to set

$$K_1(Q) = -f(Q/C). \quad (4.4.64)$$

Then, after the substitution of (4.4.64) into (4.4.62), we arrive at

$$\kappa_1(x) = -(S/C)(2\pi kTC)^{-1/2} \int_0^\infty \exp[-\frac{1}{2}\beta C^{-1}(Q - xC)^2] Q dQ. \quad (4.4.65)$$

Putting $x = 0$ gives

$$\begin{aligned} l_1 &= \kappa_1(0) \\ &= -(S/C)(2\pi kTC)^{-1/2} \int_0^\infty \exp[-(2C)^{-1}\beta Q^2] Q dQ \\ &= -(2\pi\beta C)^{-1/2} S. \end{aligned} \quad (4.4.66)$$

We see that the necessary relation (4.1.10) is not satisfied. This means that (4.4.64) is also erroneous. To correct the situation we add the shift (4.4.66) by setting

$$K_1(Q) = -f(Q/C) + (2\pi\beta C)^{-1/2} S. \quad (4.4.67)$$

Then, instead of (4.4.63), we get

$$\begin{aligned} \kappa_1(x) &= -(S/C)(2\pi kTC)^{-1/2} \int_0^\infty \exp[-(2C)^{-1}\beta(Q - Cx)^2] Q dQ \\ &\quad + (2\pi\beta C)^{-1/2} S. \end{aligned} \quad (4.4.68)$$

In Sect. 3.3.3 we have already discussed the necessity of the vertical shift of the characteristic of the asymmetrically conducting nonlinear resistor. With the help of (4.4.68) we find the coefficient

$$l_{1,1} \equiv (d\kappa_1/dx)_{x=0} = -(S/C)(2\pi kTC)^{-1/2} \beta \int_0^\infty \exp[-2^{-1}\beta C^{-1}Q^2] Q^2 dQ \quad (4.4.69)$$

entering (4.1.12). This coefficient can be written as

$$l_{1,1} = -(\beta S/2C)\langle Q^2 \rangle, \quad (4.4.70)$$

where $\langle \dots \rangle$ means averaging with the weight (4.4.60). Hence,

$$l_{1,1} = -S/2. \quad (4.4.71)$$

By virtue of (4.3.20a) we obtain

$$K_{11}(Q) = kTS . \quad (4.4.72)$$

Thus, using the phenomenological equation (4.4.59), we have constructed the Fokker–Planck operator

$$-\frac{\partial}{\partial Q} K_1(Q) + \frac{kTS}{2} \frac{\partial^2}{\partial Q^2} , \quad (4.4.73)$$

where $K_1(Q)$ is given by (4.4.67). We can also take the linear function $l_{1,1}x(Q)$ instead of (4.4.67). In doing so the error increases. In this case the phenomenological equation takes the form

$$\dot{Q} = -\frac{1}{2}(S/C)Q , \quad (4.4.74)$$

and, according to (4.4.21), one can find the correlation function of charge fluctuation:

$$\langle Q(t + \tau)Q(t) \rangle = kTC \exp[-(2C)^{-1}S\tau] \quad \text{for } \tau > 0 . \quad (4.4.75)$$

A more exact consideration in which nonzero values of $l_{1,11}$ and $l_{1,111}$ are taken into account is also possible.

The above approximate method of avoiding the nonlinearity can be called the method of statistical linearization. It can also be applied in other cases of analyticity breaks, say, in the case of a particle with “dry” friction: $f_{fr} = -f_0 v/v$ (f_{fr} is the frictional force and v is the particle velocity). Unlike (4.4.71), in this case $l_{1,1}$ depends on temperature.

4.4.6 The Mechanical Oscillator

Let a body of mass m hang on a spring with rigidity κ (Fig. 4.4). Denoting the deviation of the body from the equilibrium by y and taking into account the frictional force, which is proportional to velocity, we obtain the phenomenological equation of motion

$$m\ddot{y} + \gamma\dot{y} + \kappa y = 0 , \quad (4.4.76)$$

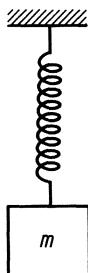


Fig. 4.4. Body of mass m suspended by a spring

where γ is the coefficient of friction. Writing $\dot{y} = v$, we have

$$m\dot{v} = -\gamma v - \kappa y. \quad (4.4.77)$$

Let us regard y and the momentum $p = mv$ as the internal parameters A_1 and A_2 . Taking into consideration the kinetic energy of the body and the energy of the spring, we write the total energy

$$U(y, p) = p^2/2m + \frac{1}{2}\kappa y^2. \quad (4.4.78)$$

In the present case the free energy $F(y, p)$ coincides with (4.4.78). Applying (3.1.38), we find the parameters conjugate to y and p :

$$\begin{aligned} x_1 &= \kappa y, \\ x_2 &= p/m = v. \end{aligned} \quad (4.4.79)$$

Using (4.4.79), we can write (4.4.77) in the standard form

$$\begin{aligned} \dot{y} &= x_2, \\ \dot{p} &= -x_1 - \gamma x_2. \end{aligned} \quad (4.4.80)$$

Here only the conjugates appear on the right-hand sides. Equations (4.4.80) are a special case of (4.4.32). From (4.4.80) we have

$$\|l_{\alpha, \beta}\| = \begin{pmatrix} 0 & 1 \\ -1 & -\gamma \end{pmatrix}. \quad (4.4.81)$$

From this we see that the relation

$$l_{1,2} = -l_{2,1} \quad (4.4.82)$$

holds. The same relation follows from (4.1.13). In our case y is a time-even variable, so that $\varepsilon_1 = 1$, and p is a time-odd variable ($\varepsilon_2 = -1$). Therefore, $\varepsilon_1 \varepsilon_2 = -1$ and (4.1.13) gives (4.4.81).

If on the right-hand side of (4.4.80) the variables x_1 and x_2 are expressed in terms of y and p , we arrive at

$$\dot{y} = m^{-1}p, \quad \dot{p} = -\kappa y - \gamma m^{-1}p. \quad (4.4.83)$$

These equations are an example of (3.1.18), and (4.4.78) is a special case of (3.1.19). Comparing general and specific formulas, we obtain

$$\begin{aligned} \hat{D} &= \|d_{\alpha\beta}\| = \begin{pmatrix} 0 & -m^{-1} \\ \kappa & \gamma m^{-1} \end{pmatrix}, \\ \hat{U} &= \|u_{\alpha\beta}\| = \begin{pmatrix} \kappa & 0 \\ 0 & m^{-1} \end{pmatrix}. \end{aligned} \quad (4.4.84)$$

Substituting (4.4.84) into (4.4.23) yields

$$\hat{F}(p) = kT \begin{pmatrix} p & -m^{-1} \\ \kappa & p + \gamma m^{-1} \end{pmatrix}^{-1} \begin{pmatrix} \kappa^{-1} & 0 \\ 0 & m \end{pmatrix}. \quad (4.4.85)$$

Calculating the inverse matrix, we get

$$F(p) = kT(p^2 + p\gamma m^{-1} + \kappa m^{-1})^{-1} \begin{pmatrix} (p + \gamma m^{-1})\kappa^{-1} & 1 \\ -1 & pm \end{pmatrix}. \quad (4.4.86)$$

Using (4.4.24), we easily find the spectral density matrix. Restricting ourselves to its diagonal elements, we have from (4.4.86)

$$\begin{aligned} S_{11}(\omega) &\equiv S_y(\omega) = F_{11}(i\omega) + F_{11}(-i\omega) = 2kT\gamma Q^{-1}(\omega), \\ S_{22}(\omega) &\equiv S_p(\omega) = F_{22}(i\omega) + F_{22}(-i\omega) = 2kT\gamma m^2\omega^2 Q^{-1}(\omega), \end{aligned} \quad (4.4.87)$$

where $Q(\omega) = (\kappa - m\omega^2)^2 + \gamma^2\omega^2$.

Many other processes in linear systems, for example, in the electric oscillatory circuit, can be analysed in the same way.

4.4.7 Field Case: Maxwell's Equations and Their Treatment from the Viewpoint of Nonequilibrium Thermodynamics

As is generally known, the following vector fields are essential in electrodynamics: the electric field strength \mathbf{E} , the magnetic field strength \mathbf{H} , the electric displacement \mathbf{D} and the magnetic induction \mathbf{B} . We will not restrict ourselves to the case of linear electrodynamics. We will regard the fields \mathbf{D} and \mathbf{B} as the fundamental ones. In this example we will treat the pair $\mathbf{D}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ as a "vector" of internal parameters A . Consequently, the subscript α now has the meaning of the pair $(m; \mathbf{r})$, where \mathbf{r} is the radius vector, and m is a subscript that runs through the values from 1 to 6, corresponding to the components of the "vector" $(D_1, D_2, D_3, B_1, B_2, B_3)$.

We suppose that the internal energy density $u(\mathbf{D}, \mathbf{B})$ is given as a function of \mathbf{D} and \mathbf{B} . This density, which does not explicitly depend on the radius vector \mathbf{r} or on time, determines the total energy

$$U[\mathbf{D}(\mathbf{r}), \mathbf{B}(\mathbf{r})] = \int u(\mathbf{D}(\mathbf{r}), \mathbf{B}(\mathbf{r})) d\mathbf{r}. \quad (4.4.88)$$

As is well known, in linear electrodynamics this density is of the form

$$u(\mathbf{D}, \mathbf{B}) = \frac{1}{2}\varepsilon_{ik}^{-1}D_iD_k + \frac{1}{2}\mu_{ik}^{-1}B_iB_k. \quad (4.4.89)$$

In the general case the fields $\mathbf{E}(\mathbf{r})$ and $\mathbf{H}(\mathbf{r})$ are defined by

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= \frac{\partial u}{\partial \mathbf{D}} = \frac{\delta U}{\delta \mathbf{D}(\mathbf{r})}, \\ \mathbf{H}(\mathbf{r}) &= \frac{\partial u}{\partial \mathbf{B}} = \frac{\delta U}{\delta \mathbf{B}(\mathbf{r})}. \end{aligned} \quad (4.4.90)$$

They are the thermodynamic forces with respect to $\mathbf{D}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$, i.e.

$$(x_\alpha) = (\mathbf{E}(\mathbf{r}), \mathbf{H}(\mathbf{r})). \quad (4.4.91)$$

In the present case the phenomenological equations in the standard form

$\dot{A}_\alpha = \kappa_\alpha(x)$ are Maxwell's equations

$$\begin{aligned}\dot{\mathbf{D}} &= \operatorname{curl} \mathbf{H} - \mathbf{j}(\mathbf{E}), \\ \dot{\mathbf{B}} &= \operatorname{curl} \mathbf{E}.\end{aligned}\quad (4.4.92)$$

The dependence of the current density \mathbf{j} on the field \mathbf{E} is determined by the constitutive relation. Using (4.4.90), we find

$$\frac{d}{dt} U = \int d\mathbf{r} \left[\frac{\delta U}{\delta \mathbf{D}} \cdot \dot{\mathbf{D}} + \frac{\delta U}{\delta \mathbf{B}} \cdot \dot{\mathbf{B}} \right] = \int [\mathbf{E} \cdot \dot{\mathbf{D}} + \mathbf{H} \cdot \dot{\mathbf{B}}] d\mathbf{r}. \quad (4.4.93)$$

Substituting (4.4.92) into (4.4.93), we easily obtain

$$\frac{d}{dt} U = \int [\mathbf{E} \cdot \operatorname{curl} \mathbf{H} - \mathbf{H} \cdot \operatorname{curl} \mathbf{E} - \mathbf{E} \cdot \mathbf{j}] d\mathbf{r} = - \int \mathbf{E} \cdot \mathbf{j} d\mathbf{r} \quad (4.4.94)$$

(the surface integral is omitted).

Consequently, in the absence of conduction in the medium there are no energy losses, as indeed must be the case. This is a confirmation of the definition (4.4.90) of \mathbf{E} and \mathbf{H} in the case of nonlinear electrodynamics.

In the framework of linear nonequilibrium thermodynamics the dependence $\mathbf{j}(\mathbf{E})$ in (4.4.92) should be taken as a linear one:

$$j_k = \sigma_{kl} E_l \quad (4.4.95)$$

Then, equations (4.4.92) assume the standard form $\dot{A}_\alpha = l_{\alpha\beta} x_\beta$ with $l_{\alpha\beta}$ given by

$$\| l_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \| = \begin{pmatrix} F & G \\ W & 0 \end{pmatrix} \delta(\mathbf{r} - \mathbf{r}'), \quad (4.4.96)$$

where F, G, W are 3×3 matrices:

$$F = -\| \sigma_{ki} \|, \quad G = \| \varepsilon_{kli} \nabla_l \|, \quad W = -G \quad (4.4.97)$$

and ε_{kli} is the completely antisymmetric tensor defined by

$$(\operatorname{curl} \mathbf{H})_k = \varepsilon_{kli} \nabla_l H_i. \quad (4.4.98)$$

We now write down the Onsager–Casimir relations (4.1.13) for the equations $\dot{A}_\alpha = l_{\alpha\beta} x_\beta$ in the present case, i.e. for Maxwell's equations

$$\dot{\mathbf{D}} = \operatorname{curl} \mathbf{H} - \hat{\sigma} \mathbf{j}, \quad \dot{\mathbf{B}} = -\operatorname{curl} \mathbf{E} \quad (\hat{\sigma} = \| \sigma_{ki} \|). \quad (4.4.99)$$

The continuity of the number of variables A_α does not violate the validity of the relations derived previously. Since the first three components of the vector $(D_1, D_2, D_3, B_1, B_2, B_3)$ have the same time parity (they are all even), the Onsager relations

$$l_{k,m}(\mathbf{r}, \mathbf{r}') = l_{m,k}(\mathbf{r}', \mathbf{r}), \quad k, m = 1, 2, 3, \quad (4.4.100)$$

i.e. by virtue of (4.4.96, 97) the relations $\sigma_{km} = \sigma_{mk}$, must be satisfied. Further, the components B_1, B_2, B_3 are time-odd and, therefore, they have the opposite parity to D_1, D_2, D_3 . Hence, the relations

$$l_{k,3+m}(\mathbf{r}, \mathbf{r}') = -l_{3+m,k}(\mathbf{r}', \mathbf{r}), \quad k, m = 1, 2, 3 \quad (4.4.101)$$

must be satisfied. Using (4.4.96, 97), we can readily check that these relations are automatically satisfied due to the structure of Maxwell's equations. Though equations (4.4.99) are related to linear nonequilibrium thermodynamics, they can also describe nonlinear electrodynamic processes since the dependences \mathbf{D} on \mathbf{E} and \mathbf{B} on \mathbf{H} can be nonlinear.

In conclusion we note that a negligible role of thermal conduction and heat exchange has been implicitly assumed in the above consideration. In reality one has the formula

$$du = Tds + \mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B}, \quad (4.4.102)$$

where s is the entropy density. From (4.4.102) it is apparent that one should take the adiabatic (isentropic) derivatives in (4.4.90). When the heat exchange is considerable and the electrodynamic processes can be assumed to be isothermal, one should replace u by the free energy density $f = u - Ts$, for which we have

$$df = -sdT + \mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B}. \quad (4.4.103)$$

In this case, (4.4.90) should be replaced by the formulas

$$\begin{aligned} \mathbf{E} &= \left(\frac{\partial f}{\partial \mathbf{D}} \right)_{T, \mathbf{B}} = \left(\frac{\delta F}{\delta \mathbf{D}} \right)_{T, \mathbf{B}}, \\ \mathbf{H} &= \left(\frac{\partial f}{\partial \mathbf{B}} \right)_{T, \mathbf{D}} = \left(\frac{\delta F}{\delta \mathbf{B}} \right)_{T, \mathbf{D}}, \end{aligned} \quad (4.4.104)$$

which contain the isothermal derivatives. There will be no other changes in the above relations.

4.4.8 Simple Chemical Reactions

Let us consider the reaction



According to (3.4.5) the molar concentrations $c_j = [E_j]$ satisfy the equations

$$\dot{c}_1 = -\frac{1}{2}\dot{c}_2 = -k_1 c_1 + k_{-1} c_2^2. \quad (4.4.106)$$

We now take into account the diffusion of reagents. Let the gases E_1 and E_2 have diffusion coefficients D_1 and D_2 , respectively. Then instead of (4.4.106) we have

$$\begin{aligned} \dot{c}_1 &= -kc_1 + k_{-1}c_2^2 + D_1 \Delta c_1, \\ \dot{c}_2 &= 2k_1 c_1 - 2k_{-1} c_2^2 + D_2 \Delta c_2. \end{aligned} \quad (4.4.107)$$

Using (3.4.25), we can write these equations in the standard form

$$\begin{aligned} \dot{c}_1 &= -k'_1 e^{\alpha x_1} + k'_{-1} e^{2\alpha x_2} + D'_1 \Delta e^{\alpha x_1}, \\ \dot{c}_2 &= 2k'_1 e^{\alpha x_1} - 2k'_{-1} e^{2\alpha x_2} + D'_2 \Delta e^{\alpha x_2}, \end{aligned} \quad (4.4.108)$$

where

$$k'_1 = c_1^0 k_1, \quad k'_{-1} = (c_2^0)^2 k_{-1}, \quad D'_1 = c_1^0 D_1, \quad D'_2 = c_2^0 D_2, \quad \alpha^{-1} = RT. \quad (4.4.109)$$

Equations (4.4.108) are a particular case of (4.3.9). Linearizing them with respect to x_1 and x_2 gives the equations

$$\begin{aligned} \dot{x}_1 &= -\alpha k'_1 x_1 + 2\alpha k'_{-1} x_2 + \alpha D'_1 \Delta x_1, \\ \dot{x}_2 &= 2\alpha k'_1 x_1 - 4\alpha k'_{-1} x_2 + \alpha D'_2 \Delta x_2, \end{aligned} \quad (4.4.110)$$

which are a specific case of (4.4.32). Since c_1 and c_2 are time-even, the reciprocal relations (4.1.13) are now of the form

$$2\alpha k'_{-1} = 2\alpha k'_1. \quad (4.4.111)$$

This equation coincides with (3.4.41), which has been discussed in Sect. 3.4. From (4.4.107) we see that the spatially constant equilibrium gas concentrations c_1^0, c_2^0 must satisfy the equation

$$k_1 c_1^0 = k_{-1} (c_2^0)^2. \quad (4.4.112)$$

This equation is equivalent to (4.4.111).

Let δ_1 and δ_2 be the deviations of the concentrations from their equilibrium values. Substituting $c_i = c_i^0 + \delta_i$ into (4.4.107) and performing the linearization in δ_1 and δ_2 , we obtain the linear equations

$$\begin{aligned} \dot{\delta}_1 &= -\beta \delta_1 + \gamma \delta_2 + D_1 \Delta \delta_1, \\ \dot{\delta}_2 &= 2\beta \delta_1 - 2\gamma \delta_2 + D_2 \Delta \delta_2, \end{aligned} \quad (4.4.113)$$

where $\beta = k_1$ and $\gamma = 2k_{-1} c_2^0$.

Equations (4.4.113) are an example of (3.1.18). Here $\delta_1(\mathbf{r})$ and $\delta_2(\mathbf{r})$ play the role of A_α , i.e. the subscript α is the pair (i, \mathbf{r}) . According to (4.4.20) we have

$$u_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \partial x_i(\mathbf{r}_1) / \partial c_j(\mathbf{r}_2). \quad (4.4.114)$$

Substituting (3.4.25), i.e.

$$x_i(\mathbf{r}) = RT \ln [c_i(\mathbf{r})/c_i^0] \quad (4.4.115)$$

into (4.4.114) yields

$$u_{ij}(\mathbf{r}_1, \mathbf{r}_2) = (RT/c_i^0) \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta_{ij}. \quad (4.4.116)$$

To avoid the differential operator Δ in (4.4.113), it is convenient to switch over to the spatial spectra

$$\delta_j(\mathbf{k}) = (2\pi)^{-3/2} \int \exp(i\mathbf{k} \cdot \mathbf{r}) \delta_j(\mathbf{r}) d\mathbf{r}. \quad (4.4.117)$$

Instead of (4.4.113) we get

$$\begin{aligned} \delta_1(\mathbf{k}) &= -(\beta + D_1 k^2) \delta_1 + \gamma \delta_2, \\ \delta_2(\mathbf{k}) &= 2\beta \delta_1 - (2\gamma + D_2 k^2) \delta_2, \end{aligned} \quad (4.4.118)$$

and instead of the matrix (4.4.116) we have

$$\hat{U} = \left\| \frac{RT}{c_i^0} \delta(\mathbf{k}_1 + \mathbf{k}_2) \delta_{ij} \right\|. \quad (4.4.119)$$

Comparing (4.4.118) with (3.1.18) gives

$$\hat{D} = \left\| \begin{pmatrix} \beta + D_1 k_1^2 & -\gamma \\ -2\beta & 2\gamma + D_2 k_1^2 \end{pmatrix} \delta(\mathbf{k}_1 + \mathbf{k}_2) \right\|. \quad (4.4.120)$$

Using (4.4.119, 120), according to (4.4.23), we obtain

$$\begin{aligned} \hat{F}(p) &= N_A^- [(p + D_1 k_1^2 + \beta)(p + D_2 k_1^2 + 2\gamma) - 2\beta\gamma]^{-1} \\ &\times \begin{pmatrix} (p + D_2 k_1^2 + 2\gamma)c_1^0 & \gamma c_2^0 \\ 2\beta c_1^0 & (p + D_1 k_1^2 + \beta)c_2^0 \end{pmatrix} \delta(\mathbf{k}_1 + \mathbf{k}_2). \end{aligned} \quad (4.4.121)$$

Furthermore, with the help of (4.4.24) one can find the temporal spectral densities for spectra (4.4.117). In Appendix 6 it is shown that the temporal spectral density of a random spatial spectrum is simply related to the space-time spectral density; see (A6.15). Considering (4.4.24) and (A6.15) and using (4.4.121), we can easily find the space-time spectral density of the processes $\delta_i(\mathbf{r}, t)$, i.e. of $c_i(\mathbf{r}, t)$. We give the final formula for the spectral density of the process $c_1(\mathbf{r}, t)$:

$$\begin{aligned} S_{c_1}(\mathbf{k}, \omega) &= 2N_A^- c_1^0 \{ (D_2 k^2 + 2\gamma)[D_1 D_2 k^4 + (2\gamma D_1 + \beta D_2)k^2 - \omega^2] \\ &+ \omega^2[(D_1 + D_2)k^2 + \beta + 2\gamma] \} \\ &\times \{ [D_1 D_2 k^4 + (2\gamma D_1 + \beta D_2)k^2 - \omega^2]^2 \\ &+ \omega^2[(D_1 + D_2)k^2 + \beta + 2\gamma]^2 \}^{-1}. \end{aligned} \quad (4.4.122)$$

The spectral density of the fluctuations $c_2(\mathbf{r}, t)$ is of a similar form. In order to obtain it we must replace the subscript 1 by the subscript 2 and also interchange β and 2γ in (4.4.122).

4.4.9 Thermal Fluctuations of the Velocity of a Liquid or Gas

As is well known, when the viscosity is taken into account, the phenomenological equation of a liquid or gas has the form

$$\rho[\dot{\mathbf{v}} + (\mathbf{v}\nabla)\mathbf{v}] = -\text{grad } p + \eta\Delta\mathbf{v} + (\zeta + 3^{-1}\eta)\text{grad div } \mathbf{v} \quad (4.4.123)$$

(see, for example, [4.4]). Here \mathbf{v} is the velocity vector depending on the radius vector \mathbf{r} ; ρ and p are the density and the pressure, respectively; η and ζ are the constant viscosity coefficients. The continuity equation

$$\dot{\rho} = -\text{div}(\rho\mathbf{v}). \quad (4.4.124)$$

must be combined with (4.4.123). Let $\rho_0, p_0, v = 0$ be the equilibrium values. Convection is assumed to be absent at equilibrium; p_0 and ρ_0 are independent of \mathbf{r} . We will consider small fluctuations of velocity, density and pressure. Linearizing

(4.4.123, 124) in v , $p' = p - p_0$ and $\rho' = \rho - \rho_0$, we arrive at

$$\dot{v} = -\rho_0^{-1} \operatorname{grad} p' + \eta \rho_0^{-1} \Delta v + (\zeta + 3^{-1}\eta) \rho_0^{-1} \operatorname{grad} \operatorname{div} v, \quad (4.4.125a)$$

$$\dot{\rho}' = -\rho_0 \operatorname{div} v. \quad (4.4.125b)$$

The kinetic energy of a liquid or gas has the form

$$K[v(r)] = \frac{1}{2} \rho_0 \int v^2(r) dr. \quad (4.4.126)$$

Substituting this energy for F into (3.1.38), i.e. into

$$x_i(r) = \delta F[v]/\delta v_i(r), \quad i = 1, 2, 3, \quad (4.4.127)$$

we find the parameters conjugate to $v_1(r)$, $v_2(r)$, $v_3(r)$:

$$x_i(r) = \rho_0 v_i(r), \quad i = 1, 2, 3. \quad (4.4.128)$$

Let us now find the parameter $x_4(r)$ conjugate to $\rho'(r)$. We will neglect heat conduction in the liquid (or gas). Then, instead of F in (4.1.38) we should take the function $H = U + p_0 V$ depending on $\rho'(r)$:

$$x_4(r) = (\partial H/\partial \rho')_s = (\partial H[\rho(r)]/\partial \rho(r))_s. \quad (4.4.129)$$

The differentiation is carried out at constant entropy density $s(r)$.

Let us divide the space into small separate cells with volume ΔV_α ; $H[\rho]$ is equal to the sum ΣH_α over the separate subvolumes. The thermodynamic equations

$$dU_\alpha = T_\alpha dS_\alpha - p_\alpha d(\Delta V_\alpha), \quad (4.4.130a)$$

$$dH_\alpha = T_\alpha dS_\alpha - p'_\alpha d(\Delta V_\alpha) \quad (4.4.130b)$$

are valid for each subvolume. If ΔM_α is the mass of the liquid in ΔV_α , then

$$\Delta V_\alpha = \Delta M_\alpha / \rho_\alpha. \quad (4.4.131)$$

Therefore,

$$d(\Delta V_\alpha) = -\rho_\alpha^{-2} \delta \rho_\alpha \Delta M_\alpha = -\rho_\alpha^{-1} \delta \rho_\alpha \Delta V_\alpha. \quad (4.4.132)$$

Here we have supposed that the cells under study always contain a constant mass of liquid and that they are deformed when ρ_α varies.

Substituting (4.4.132) into (4.4.130b), summing over the different cells and passing to the limit $\max \Delta V_\alpha \rightarrow 0$, we obtain

$$\delta H[\rho(r)] = \int T \delta s(r) dr + \int \frac{p'}{\rho} \delta \rho(r) dr \quad (s = dS/dV). \quad (4.4.133)$$

Hence, according to (4.4.129) we find

$$x_4(r) = \rho^{-1}(r) \rho'(r) \approx \rho_0^{-1} p'(r). \quad (4.4.134)$$

If the variables p' , v on the right-hand side of (4.4.125) are expressed in terms of $x_i(r)$ ($i = 1, \dots, 4$) by using (4.4.128, 134), we obtain the equations in the standard form

$$\dot{v} = -\operatorname{grad} x_4 + \eta \rho_0^{-2} \Delta x + (\zeta + 3^{-1}\eta) \rho_0^{-2} \operatorname{grad} \operatorname{div} x, \quad (4.4.135)$$

$$\dot{\rho} = -\operatorname{div} x.$$

Using the same method as in Sect. 4.4.7, we easily verify that the reciprocal relations (4.1.13) are satisfied for them.

Let us now return to (4.4.125) and replace p' by $\rho'[(\partial p/\partial\rho)_s]_{p=p_0}$ in (4.4.125a). Proceeding from $\mathbf{v}(\mathbf{r})$ and $\rho'(\mathbf{r})$ to the spatial spectra $\mathbf{v}(\mathbf{k})$ and $\rho'(\mathbf{k})$, which are defined in analogy to (4.4.117), gives

$$\begin{aligned}\dot{\mathbf{v}}(\mathbf{k}) &= \alpha i \mathbf{k} \rho'(\mathbf{k}) - \eta \rho_0^{-1} k^2 \mathbf{v} - (\zeta + 3^{-1}\eta) \rho_0^{-1} \mathbf{k} (\mathbf{k} \cdot \mathbf{v}), \\ \dot{\rho}'(\mathbf{k}) &= \rho_0 i \mathbf{k} \cdot \mathbf{v},\end{aligned}\quad (4.4.136)$$

where $\alpha = \rho_0^{-1}(\partial p/\partial\rho)_s$.

If we introduce the longitudinal and transverse velocities

$$\begin{aligned}v_{||} &= (\mathbf{k} \cdot \mathbf{v})/k, \\ v_{\perp} &= \mathbf{v} - \frac{\mathbf{k}}{k} v_{||},\end{aligned}\quad (4.4.137)$$

the set of equations (4.4.136) splits into two independent parts. One equation determines the transverse velocity

$$\dot{v}_{\perp}(\mathbf{k}) = -\eta \rho_0^{-1} k^2 v_{\perp}. \quad (4.4.138)$$

The other part is the set of equations

$$\begin{aligned}\dot{v}_{||}(\mathbf{k}) &= \alpha i \mathbf{k} \rho'(\mathbf{k}) - \eta \rho_0^{-1} k^2 v_{||}, \\ \dot{\rho}' &= \rho_0 i k v_{||},\end{aligned}\quad (4.4.139)$$

where $\zeta' = \zeta + 4\eta/3$.

Formula (4.4.126) has an analogous form for the spectrum $\mathbf{v}(\mathbf{k})$:

$$K = \frac{1}{2} \rho_0 \int v^2(\mathbf{k}) d\mathbf{k}. \quad (4.4.140)$$

By virtue of (4.4.137) it can be represented as a sum of the terms

$$K = \frac{1}{2} \rho_0 \int v_{\perp}^2(\mathbf{k}) d\mathbf{k} + \frac{1}{2} \rho_0 \int v_{||}^2(\mathbf{k}) d\mathbf{k}, \quad (4.4.141)$$

corresponding to longitudinal and transverse velocities. From (4.4.141) we obtain the transverse and longitudinal matrices (4.4.20):

$$\hat{U}_{\perp} = \|\rho_0 \delta_{ij}\|, \quad u_{||} = \rho_0. \quad (4.4.142)$$

Using (4.4.138, 139, 142), according to (4.4.15) we can easily find the space-time spectral density of velocities. It consists of the transverse and longitudinal parts:

$$S_{ij}(\omega, \mathbf{k}) = \left(\delta_{ij} - \frac{k_i k_j}{k^2} \right) S_{\perp}(\omega, \mathbf{k}) + \frac{k_i k_j}{k^2} S_{||}(\omega, \mathbf{k}). \quad (4.4.143)$$

For small compressibility the main contribution is made by the transverse part. Let us find this part. From (4.4.138, 142, 5) we have $\hat{D} = \eta \rho_0^{-1} k^2 \hat{I}_2$ and

$\hat{L} = \hat{L}^0 = -\eta\rho_0^{-2}k^2\hat{I}_2$, where $\hat{I}_2 = \hat{I} - \mathbf{k}\cdot\mathbf{k}^T/k^2$. Using (4.4.15) gives

$$S_{ik_1, jk_2}^\perp(\omega) = k_B T \frac{2\eta k^2}{\omega^2 \rho_0^2 + \eta^2 k^4} \delta_{ij} \delta(\mathbf{k}_1 + \mathbf{k}_2). \quad (4.4.144)$$

Applying formula (A6.15), which relates the temporal spectral density of the spatial spectrum to the space-time spectral density, we obtain from (4.4.144)

$$S_\perp(\mathbf{k}, \omega) = k_B T \frac{2\eta k^2}{\rho_0^2 \omega^2 + \eta^2 k^4}. \quad (4.4.145)$$

This equation should be substituted into (4.4.143).

In conclusion of this section we note that, using the stochastic equation (4.3.22) or the master equation, in the linear approximation we can also find the non-equilibrium correlators and moments. The nonequilibrium nature of correlators can be caused, for instance, by the nonequilibrium initial conditions for internal parameters.

4.5 Examples of the Application of the Markov FDRs of Nonlinear Nonequilibrium Thermodynamics

4.5.1 Simple Circuit with a Capacitor and a Nonlinear Resistor

Let us consider the circuit in Fig. 4.2, but instead of (4.4.58) we will take the quadratic current-voltage characteristic of a nonlinear resistor:

$$I = f(V) = SV + \frac{1}{2}\gamma V^2. \quad (4.5.1)$$

Unlike in Sect. 4.4.5 we shall consider the linear-quadratic approximation. Substituting (4.5.1) into (4.4.59) gives

$$\dot{Q} = -\frac{S}{C}Q - \frac{\gamma}{2C^2}Q^2. \quad (4.5.2)$$

To obtain the standard form of the equation it is necessary to express the charge Q on the right-hand side of (4.5.2) by its conjugate

$$x = dW/dQ = Q/C. \quad (4.5.3)$$

Then we have

$$\dot{Q} = -Sx - \frac{1}{2}\gamma x^2. \quad (4.5.4)$$

This equation is a special case of (4.3.9) [when $\kappa_\alpha(x)$ are determined by (4.3.29)], and

$$l_{1,1} = -S, \quad l_{1,11} = -\gamma. \quad (4.5.5)$$

Applying (4.3.25, 26) and taking into account that the parameter Q is time-even, we arrive at

$$K_{11}(Q) = 2kTS + kT\gamma Q/C , \quad (4.5.6a)$$

$$K_{111}(Q) = 0 . \quad (4.5.6b)$$

Further, as a consequence of (4.5.5), we find from (4.3.31)

$$K_\alpha(Q) = -\frac{SQ}{C} - \frac{\gamma Q^2}{2C^2} + kT \frac{\gamma}{2C} . \quad (4.5.7)$$

By virtue of (4.5.6, 7) this system is described by the master equation

$$\dot{w}(Q) = L_1 w(Q) + \frac{\gamma}{2C} \frac{\partial}{\partial Q} \left[\left(\frac{Q^2}{C} - kT \right) w(Q) \right] + \frac{kT\gamma}{2C} \frac{\partial^2}{\partial Q^2} [Qw(Q)] , \quad (4.5.8)$$

which is a special case of (2.3.24). Here

$$L_1 = \frac{\partial}{\partial Q} \frac{SQ}{C} + kTS \frac{\partial^2}{\partial Q^2} \quad (4.5.9)$$

is the operator of linear approximation. In solving (4.5.8) the quantity γ can be regarded as a small parameter. Actually, the dimensionless quantity

$$\frac{\gamma\sigma}{CS} = \frac{\gamma}{S} \left(\frac{kT}{C} \right)^{1/2} \ll 1 \quad (4.5.10)$$

is the small parameter, where $\sigma^2 = \langle Q^2 \rangle = kTC$. Inequality (4.5.10) holds since the Boltzmann constant is a microscopic quantity and the other quantities have a macroscopic sense.

By using the effective transconductance S_{eff} , (4.5.6a) can be written as

$$K_{11} = 2kTS_{\text{eff}} , \quad (4.5.11)$$

where

$$S_{\text{eff}} = S + \frac{\gamma Q}{2C} = S + \frac{\gamma}{2} V . \quad (4.5.12)$$

Then, in the linear-quadratic approximation, the formula for K_{11} will be analogous to that of the linear approximation

$$K_{11} = 2kTS . \quad (4.5.13)$$

From (4.5.1, 12) it is seen that the average transconductance

$$S_{\text{av}} = [f'(0) + f'(V)]/2$$

or

$$S_{\text{av}} = V^{-1} \int_0^V f'(U) dU = f(V)/V$$

plays the role of the effective transconductance S_{eff} .

4.5.2 Circuit with an Inductor and a Nonlinear Resistor

Let us consider the circuit in which an inductor L is placed instead of capacitor (Fig. 4.5). Let the characteristic of the nonlinear resistor be given by (4.5.1). Solving (4.5.1) for V by iterations gives

$$V = g(I) = RI + \frac{1}{2}\alpha I^2 + \dots, \quad (4.5.14)$$

where

$$R = 1/S, \quad \alpha = -\gamma/S^3. \quad (4.5.15)$$

The phenomenological equation

$$L \frac{dI}{dt} = -g(I) = -RI - \frac{1}{2}\alpha I^2. \quad (4.5.16)$$

corresponds to this circuit. We take the “momentum” $p = LI$ as an internal parameter A_1 . Since the inductor energy is

$$W = \frac{1}{2}LI^2 = \frac{1}{2L}p^2, \quad (4.5.17)$$

the current I will coincide with the parameter $x = \partial W/\partial p$ conjugate to p . Hence, the standard form of (4.5.16) is written as

$$\dot{p} = -RI - \frac{1}{2}\alpha I^2. \quad (4.5.18)$$

This equation is another special case of (4.3.9) with $\kappa_\alpha(x)$ determined by (4.3.29) for $l_{1,1} = -R$ and $l_{1,11} = -\alpha$. Using (4.3.25, 26) and taking into account time-oddness of the “momentum” p , we find

$$K_{11}(p) = 2kTR + 3kT\alpha p/L, \quad (4.5.19a)$$

$$K_{111}(p) = -6(kT)^2\alpha. \quad (4.5.19b)$$

Applying (4.3.31) yields

$$K_1(p) = -\frac{R}{L}p - \frac{\alpha p^2}{2L^2} + \frac{kT\alpha}{2L}. \quad (4.5.20)$$

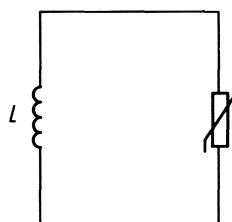


Fig. 4.5. Simple circuit with inductor and nonlinear resistor

Thus, in the circuit under study the fluctuation-relaxation process is described by the equation

$$\begin{aligned}\dot{w}(p) &= L_1 w(p) + \frac{\alpha}{2L} \frac{\partial}{\partial p} \left[\left(\frac{p^2}{L} - kT \right) w \right] \\ &\quad + \frac{3kT\alpha}{2L} \frac{\partial^2(pw)}{\partial p^2} + (kT)^2 \alpha \frac{\partial^3 w}{\partial p^3},\end{aligned}\quad (4.5.21)$$

where

$$L_1 = \frac{R}{L} \frac{\partial}{\partial p} p + kTR \frac{\partial^2}{\partial p^2} \quad (4.5.22)$$

is the operator of the linear approximation. Equation (4.5.21) is not the Fokker-Planck equation. By analogy with the formula of the linear approximation, (4.5.19a) can be written as

$$K_{11} = 2kTR_{\text{eff}}. \quad (4.5.23)$$

The effective resistance

$$R_{\text{eff}} = R + \frac{3}{2}\alpha I \quad (4.5.24)$$

now does not coincide with the average resistance $R_{\text{av}} = V(I)/I$, but it coincides with the resistance

$$R_1 = \frac{1}{2} \partial^2(IV(I)) / \partial I^2. \quad (4.5.25)$$

As a consequence of the formula

$$K_{11}(LI) = \lim_{\tau \rightarrow 0} [\tau^{-1} \langle (\Delta p)^2 \rangle_I] \quad (4.5.26)$$

[see (2.3.25)], (4.5.23, 24) determine the correlation function

$$\langle \xi(t_1) \xi(t_2) \rangle = 2kT [R + \frac{3}{2}\alpha I + O(I^2)] \delta(t_1 - t_2) \quad (4.5.27)$$

of the random noise $\xi(t)$ appearing in

$$L dI/dt = K_1(LI) + \xi(t). \quad (4.5.28)$$

From this equation it is seen that $\xi(t)$ has the sense of a random e.m.f. arising in a nonlinear resistor when a current flows through it. Formula (4.5.27) is also valid when the constant current flowing through the nonlinear resistor is induced by a voltage source (say, by an electrical element) brought into the circuit. The noise $\xi(t)$ cannot be regarded as Gaussian since in that case the term with the third derivative would be absent in (4.5.21).

4.5.3 Heat Exchange of Two Bodies in the Linear-Quadratic Approximation

In the preceding examples the relaxation equations (4.3.1) were nonlinear and the energy was quadratic in the internal parameters. Let us now consider an example where the dependence of thermodynamic force X on the internal parameter contains a nonlinear term.

In the general case the heat exchange of two bodies can be described by

$$dQ/dt = f(T_1, T_2)(T_2 - T_1), \quad (4.5.29)$$

where $f(T_1, T_2)$ is some function. The multiplier $(T_2 - T_1)$ is separated from $f(T_1, T_2)$ to emphasize the fact that the heat influx dQ/dt is equal to zero when $T_1 = T_2$. As in Sect. 4.4.3, we will denote the internal energies of the two bodies by U_1 and U_2 , so that $\dot{U}_1 = -\dot{U}_2 = dQ/dt$. We suppose that the condition of thermal isolation $U_1 + U_2 = \text{const}$ is fulfilled. In accordance with (4.4.42) we have $dS = (T_1^{-1} - T_2^{-1})dU_1$, so that

$$X = -dS/dU_1 = T_2^{-1} - T_1^{-1}. \quad (4.5.30)$$

If the heat capacities c_1 and c_2 of the bodies depend on the temperature, the equilibrium temperature Θ is determined by the equation

$$\int_{\Theta}^{T_1} c_1(T) dT + \int_{\Theta}^{T_2} c_2(T) dT = 0, \quad (4.5.31)$$

which describes the energy balance.

Substituting the expansions $c_i(T) = c_i + c'_i(T - \Theta)$, where $c_i = c_i(\Theta)$ and $c'_i = c'_i(\Theta)$, into (4.5.31) yields

$$c_1(T_1 - \Theta) + c_2(T_2 - \Theta) + \frac{1}{2}c'_1(T_1 - \Theta)^2 + \frac{1}{2}c'_2(T_2 - \Theta)^2 = 0. \quad (4.5.32)$$

Using this equation, we can express $T_2 - \Theta$ by $T_1 - \Theta$ and then subtract $T_1 - \Theta$ from $T_2 - \Theta$. We arrive at

$$T_1 = \Theta + \frac{c_2}{c_1 + c_2}(T_1 - T_2) - \frac{c'_1 c_2^2 + c'_2 c_1^2}{2(c_1 + c_2)^3}(T_1 - T_2)^2 + \dots, \quad (4.5.33a)$$

$$T_2 = \Theta - \frac{c_1}{c_1 + c_2}(T_1 - T_2) - \frac{c'_1 c_2^2 + c'_2 c_1^2}{2(c_1 + c_2)^3}(T_1 - T_2)^2 + \dots. \quad (4.5.33b)$$

Substituting (4.5.33) into (4.5.29) and taking into account that $\dot{U}_1 = dQ/dt$, we find

$$\dot{U}_1 = -\lambda(T_1 - T_2) - \mu(T_1 - T_2)^2, \quad (4.5.34)$$

Here

$$\lambda = f(\Theta, \Theta), \quad \mu = \left[\frac{\partial f}{\partial T_1}(\Theta, \Theta)c_2 - \frac{\partial f}{\partial T_2}(\Theta, \Theta)c_1 \right](c_1 + c_2)^{-1}. \quad (4.5.35)$$

Further, inserting (4.5.33) into (4.5.30) and expanding the inverse temperatures in a power series of $\tau_1 = T_1 - \Theta$ and $\tau_2 = T_2 - \Theta$, we have

$$X = \frac{T_1 - T_2}{\Theta^2} + \frac{c_1 - c_2}{c_1 + c_2} \frac{(T_1 - T_2)^2}{\Theta^3}. \quad (4.5.36)$$

It is easy to solve (4.5.36) iteratively for $T_1 - T_2$. This gives

$$T_1 - T_2 = \Theta^2 X - \frac{c_1 - c_2}{c_1 + c_2} \Theta^3 X^2. \quad (4.5.37)$$

Substituting this equation into (4.5.34), we obtain the standard form of the relaxation equation:

$$\dot{U}_1 = -\lambda\Theta^2 X + \lambda \frac{c_1 - c_2}{c_1 + c_2} \Theta^3 X^2 - \mu\Theta^4 X^2 , \quad (4.5.38)$$

which is a special case of the equation $\dot{A}_\alpha = \lambda_\alpha(X)$. From (4.5.38) we can find the derivatives (4.1.32) for this case:

$$\begin{aligned} L_{1,1} &= -\lambda\Theta^2 , \\ L_{1,11} &= 2\lambda \frac{c_1 - c_2}{c_1 + c_2} \Theta^3 - 2\mu\Theta^4 . \end{aligned} \quad (4.5.39)$$

Using (4.5.39), according to (4.1.33), we get

$$\begin{aligned} L_{11} &= 2k\lambda\Theta^2 , \\ L_{111} &= 0 , \\ L_{11,1} &= -2k \left(\frac{c_1 - c_2}{c_1 + c_2} \lambda\Theta^3 - \mu\Theta^4 \right) . \end{aligned} \quad (4.5.40)$$

Now, using the formulas of the modified version, i.e. (4.3.39, 40), we can find the coefficients of the Fokker–Planck equation

$$\dot{w}(U_1) = -\frac{\partial}{\partial U_1} [K_1(U_1)w(U_1)] + \frac{1}{2} \frac{\partial^2}{\partial U_1^2} [K_{11}(U_1)w(U_1)] , \quad (4.5.41)$$

which is more precise than the equation of the linear approximation. By virtue of (4.3.39, 40), we have in our case

$$\begin{aligned} K_{11}(U_1) &= L_{11} + L_{111,1} X_1 , & K_{111} &= L_{111} , \\ K_1(U_1) &= L_{1,1} X_1 + \frac{1}{2} L_{1,11} (X_1^2 - \partial X_1 / \partial U_1) . \end{aligned} \quad (4.5.42)$$

Here we should express X by U_1 using (4.5.33a, 36) and

$$U_1 - U_1^0 = \int_{\Theta}^{T_1} c_1(T) dT = c_1(T_1 - \Theta) + \frac{1}{2} c'_1 (T_1 - \Theta)^2 . \quad (4.5.43)$$

Instead of $w(U_1)$ we can also consider the probability density of the temperature $w(T_1)$.

The Fokker–Planck equation (4.5.41) with the coefficients (4.5.42) enables us to determine the non-Gaussian characteristics of the fluctuation–dissipation process of the heat exchange. We note that, if $c_1 = c_2$, this process will be weakly non-Gaussian even in the case when the heat exchange equation is linear, i.e. when $\mu = 0$ in (4.5.34).

4.5.4 Chemical Reaction in the Linear–Quadratic Approximation

As an example, let us consider the reaction



We denote the molar concentrations of the gases N_2 , H_2 and NH_3 by c_1 , c_2 , c_3 , respectively. Then we set $C_i = Vc_i$. We will use the concept of the extent of reaction ξ . Specifying (3.4.43) for the present case, we get

$$dC_1 = -d\xi, \quad dC_2 = -3d\xi, \quad dC_3 = 2d\xi. \quad (4.5.45)$$

In our case (3.4.55) is of the form

$$\dot{\xi} = Vk_1 c_1 c_2^3 - Vk_{-1} c_3^2, \quad (4.5.46)$$

where c_1 , c_2 , c_3 are functions of ξ . The parameter \mathcal{A} , which is called the affinity, is the conjugate of the extent of reaction. By virtue of (3.4.48)

$$\mathcal{A} = 2\xi_3 + 2RT \ln c_3 - \xi_1 - RT \ln c_1 - 3\xi_2 - 3RT \ln c_2. \quad (4.5.47)$$

This expression is equal to zero at equilibrium [see (3.4.52)]. Denoting the equilibrium concentrations by c_i^0 , we can write (4.5.47) as

$$\mathcal{A} = 2RT(\ln c_3 - \ln c_3^0) - RT(\ln c_1 - \ln c_1^0) - 3RT(\ln c_2 - \ln c_2^0). \quad (4.5.48)$$

We expand (4.5.48) into a power series in $c_i - c_i^0$ and restrict ourselves to linear and quadratic terms. This gives

$$\begin{aligned} \mathcal{A} &= 2RT \left[\frac{c_3 - c_3^0}{c_3^0} - \left(\frac{c_3 - c_3^0}{c_3^0} \right)^2 \right] - RT \left[\frac{c_1 - c_1^0}{c_1^0} - \left(\frac{c_1 - c_1^0}{c_1^0} \right)^2 \right] \\ &\quad - 3RT \left[\frac{c_2 - c_2^0}{c_2^0} - \left(\frac{c_2 - c_2^0}{c_2^0} \right)^2 \right]. \end{aligned} \quad (4.5.49)$$

Integrating (4.5.45) and assuming that in the equilibrium state the parameter ξ is equal to zero, we obtain

$$C_1 - C_1^0 = -\xi, \quad C_2 - C_2^0 = -3\xi, \quad C_3 - C_3^0 = 2\xi. \quad (4.5.50)$$

Inserting these equations into equation (4.5.49) in which c_i and c_i^0 should be replaced by C_i and C_i^0 , we find

$$\mathcal{A} = RT(\lambda\xi + \gamma\xi^2), \quad (4.5.51)$$

where

$$\begin{aligned} \lambda &= 1/C_1^0 + 9/C_2^0 + 4/C_3^0, \\ \gamma &= (C_1^0)^{-2} + 27(C_2^0)^{-2} - 8(C_3^0)^{-2}. \end{aligned} \quad (4.5.52)$$

Solving (4.5.51) for ξ by iterations gives

$$\xi = \lambda^{-1}(\mathcal{A}/RT) - \lambda^{-3}\gamma(\mathcal{A}/RT)^2. \quad (4.5.53)$$

Using (4.5.48) and the equation

$$k_1 c_1^0 (c_2^0)^3 = k_{-1} (c_3^0)^2, \quad (4.5.54)$$

which is a consequence of equation (4.5.46) taken at the equilibrium point $\dot{\xi} = 0$, we can write (4.5.46) as

$$\dot{\xi} = Vk'_1 (C_3/C_3^0)^2 (e^{-\alpha\mathcal{A}} - 1), \quad (4.5.55)$$

where $k'_1 = k_1 c_1^0 (c_2^0)^3$ and $\alpha = (RT)^{-1}$.

To obtain the completely standardized equation $\dot{\xi} = \kappa(\mathcal{A})$ from (4.5.55), it remains to express

$$c_3/c_3^0 = 1 + (C_3 - C_3^0)/C_3^0 \quad (4.5.56)$$

in terms of \mathcal{A} using (4.5.50). In the linear-quadratic approximation, in (4.5.56) it is sufficient to consider only the terms constant and linear in \mathcal{A} . Expanding the exponent into a power series of \mathcal{A} gives

$$\begin{aligned} \dot{\xi} &= V k'_1 [1 + 4(\lambda C_3^0)^{-1} \alpha \mathcal{A}] (-\alpha \mathcal{A} + \frac{1}{2} \alpha^{-2} \mathcal{A}^2) \\ &= V k'_1 \left[-\alpha \mathcal{A} + \left(\frac{1}{2} - \frac{4}{\lambda C_3^0} \right) \alpha^2 \mathcal{A}^2 \right]. \end{aligned} \quad (4.5.57)$$

This equation is a special case of (4.3.9).

From (4.5.57), for the present case we find

$$l_{1,1} = -V k'_1 \alpha^{-1}, \quad l_{1,11} = V k'_1 \alpha^{-2} \left(1 - \frac{8}{\lambda C_3^0} \right). \quad (4.5.58)$$

Taking into account that for our case $\varepsilon_1 = 1$ and using (4.3.25, 26), we obtain

$$\begin{aligned} K_{11}(\xi) &= \frac{V k'_1}{N_A} \left[2 - \left(1 - \frac{8}{\lambda C_3^0} \right) \alpha \mathcal{A}(\xi) \right], \\ K_{111}(\xi) &= 0. \end{aligned} \quad (4.5.59)$$

Here it is sufficient to set $\mathcal{A}(\xi) = RT\lambda\xi$, i.e. to take only the linear term of (4.5.51).

Further, using (4.3.31) gives

$$K_1(\xi) = V k'_1 \left[-\lambda\xi - \gamma\xi^2 + \left(\frac{1}{2} - \frac{4}{\lambda C_3^0} \right) (\lambda^2 \xi^2 - N_A^{-1} \lambda) \right]. \quad (4.5.60)$$

We have thereby found the coefficients $K_1(\xi)$ and $K_{11}(\xi)$ of the Fokker-Planck equation

$$\dot{w}(\xi) = -\frac{\partial}{\partial\xi}(K_1(\xi)w) + \frac{1}{2} \frac{\partial^2}{\partial\xi^2}(K_2(\xi)w), \quad (4.5.61)$$

which are more precise than the coefficients

$$\begin{aligned} K_1(\xi) &= -V k'_1 \lambda \xi, \\ K_{11}(\xi) &= 2V N_A^{-1} k'_1 \end{aligned} \quad (4.5.62)$$

of the linear approximation. The more precise Fokker-Planck equation with coefficients (4.5.59, 60) permits one to determine, in particular, the non-Gaussian characteristics of the fluctuation-dissipation process.

Without using FDRs, the coefficient functions (4.5.59, 60) and the Fokker-Planck equation can be obtained from the master equation (3.4.56), which gives a complete description of chemical reactions for the ideal gas model. However, if the chemical reactions occur in concentrated gases or solutions, the ideal gas model is inadmissible. In this case the master equation (3.4.34) or (3.4.56) is invalid since we cannot assume that the reactions proceed by elementary statistically independent jumps, i.e. by means of the uncorrelated appearances of separate molecules. For

large concentrations, equations (3.4.5) or (3.4.55) and (3.4.25) are also invalid. In this case phenomenological equations can be obtained from experiment or by using a more exact theory. Applying the Markov FDRs, from these equations one can construct the master equation, say, in the same approximation in which (4.5.61) has been obtained.

4.5.5 Linear–Cubic Approximation: Example with Capacitance

Let us return to the circuit in Fig. 4.2 (Sect. 4.5.1). We now suppose that the nonlinear resistor has the symmetrical linear–cubic characteristic

$$I = f(V) = SV + \frac{1}{6}\lambda V^3. \quad (4.5.63)$$

The substitution of (4.5.63) into (4.4.59) leads to

$$\dot{Q} = -\frac{S}{C}Q - \frac{\lambda}{6C^3}Q^3. \quad (4.5.64)$$

Hence, using (4.5.3), we obtain the standard form of (4.5.64):

$$\dot{Q} = -Sx - \frac{1}{6}\lambda x^3 \equiv \kappa_1(x). \quad (4.5.65)$$

This equation is a special case of (4.3.9) in which the function $\kappa_\alpha(x)$ is taken in the form (4.3.33). Therefore, we have

$$l_{1,1} = -S, \quad l_{1,11} = 0, \quad l_{1,111} = -\lambda. \quad (4.5.66)$$

Using (4.1.29, 31) and (4.3.35) at $\varepsilon_1 = 1$, we get

$$\begin{aligned} K_{1111}(Q) &= 2(kT)^3(4\lambda + 3c_1), \\ K_{111}(Q) &= -(kT)^2(4\lambda + 3c_1)Q/C. \end{aligned} \quad (4.5.67)$$

Here $c_1 = c_{11,11}$ is the only dissipationally undeterminable parameter in the present case.

Further, applying (4.1.28) and (4.3.36, 37) yields

$$\begin{aligned} K_{11}(Q) &= 2kTS + \frac{1}{2}kT(2\lambda + c_1)(Q/C)^2 - \frac{1}{2}(kT)^2(2\lambda + c_1)/C, \\ K_1(Q) &= -\frac{S}{C}Q - \frac{\lambda Q^3}{6C^3} + \frac{kT\lambda Q}{2C^2}. \end{aligned} \quad (4.5.68)$$

Thus, the master equation for the charge probability density has the form

$$\begin{aligned} \dot{w}(Q) &= L_1 w + \frac{\partial}{\partial Q} \left[\left(\frac{\lambda Q^3}{6C^3} - \frac{kT\lambda Q}{2C^2} \right) w \right] + \frac{kTc_2}{4} \frac{\partial^2}{\partial Q^2} \left[\left(\frac{Q^2}{C^2} - \frac{kT}{C} \right) w \right] \\ &\quad + \frac{(kT)^2}{6C} \frac{\partial^3}{\partial Q^3} [(3c_2 - 2\lambda)Qw] + \frac{(kT)^3}{12} (3c_2 - 2\lambda) \frac{\partial^4 w}{\partial Q^4}, \end{aligned} \quad (4.5.69)$$

where $c_2 = c_1 + 2\lambda$ and

$$L_1 = \frac{S}{C} \frac{\partial}{\partial Q} Q + kTS \frac{\partial^2}{\partial Q^2} \quad (4.5.70)$$

is the operator of the linear approximation.

The solution of (4.5.69) is facilitated by the fact that the parameters λ and c_2 can be considered relatively small. More precisely, the inequalities

$$\frac{\lambda \langle Q^2 \rangle}{C^2 S} = \frac{kT\lambda}{CS} \ll 1 , \quad (4.5.71a)$$

$$\frac{kTc_2}{CS} \ll 1 \quad (4.5.71b)$$

must be valid. Though the parameter c_2 is dissipationally undeterminable, there is no doubt that (4.5.71b) holds since k is small.

4.5.6 Oscillatory Circuit

Let us consider the case when there are two internal parameters, or, in other words, the phenomenological equation is a second-order differential equation. Consider an oscillatory circuit (Fig. 4.6) with nonlinear resistance that has a symmetrical characteristic (4.5.63).

Adding the voltages across the different elements of the circuit, we obtain

$$L\ddot{Q} + g(\dot{Q}) + Q/C = 0 , \quad (4.5.72)$$

where Q is the charge on the capacitor and $V = g(I)$ is the inverse of the dependence (4.5.63). Solving (4.5.63) for V gives

$$g(I) = RI + \frac{1}{6}\gamma I^3 + \dots , \quad (4.5.73)$$

where $R = S^{-1}$ and $\gamma = -R^4\lambda$. We take Q and $p = LQ$ as the internal parameters B_1 and B_2 , respectively. The forces conjugate to them are

$$x_1 = Q/C, \quad x_2 = p/L . \quad (4.5.74)$$

From (4.5.72, 74) we easily obtain the standard equations

$$\dot{Q} = x_2 \equiv \kappa_1(x) , \quad (4.5.75a)$$

$$\dot{p} = -x_1 - Rx_2 - \frac{1}{6}\gamma x_2^3 \equiv \kappa_2(x) . \quad (4.5.75b)$$

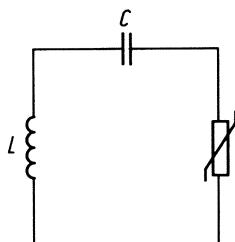


Fig. 4.6. Oscillatory circuit with nonlinear resistor

Hence, we get the values of the coefficients (4.1.6):

$$\begin{aligned} l_{1,2} &= 1, \\ l_{2,1} &= -1, \\ l_{2,2} &= -R, \\ l_{2,222} &= -\gamma. \end{aligned} \tag{4.5.76}$$

The other coefficients are equal to zero.

To determine the coefficient functions $K_\alpha(B)$, $K_{\alpha\beta}(B)$, $K_{\alpha\beta\gamma}(B)$ and $K_{\alpha\beta\gamma\delta}(B)$ of the master equation for our case, the dissipationally undeterminable matrix $c_{\alpha\beta,\gamma\delta}$ must be given in addition to (4.5.72). In the general two-component case this matrix has six independent elements [as mentioned at the end of Sect. 4.1.2, the number of independent elements decreases by virtue of (4.1.27)]. However, we have only the nonlinear dissipative element (nonlinear resistor) in our case; therefore, the number of independent dissipationally undeterminable parameters can be set equal to 1. This additional decrease of the number of parameters is ensured by the causality principle: since the nonlinear resistor is taken into account only in (4.5.75b), one can equate to zero all elements of the matrix $c_{\alpha\beta,\gamma\delta}$, except $c_{22,22} = c_2$. Then using (4.1.28, 29, 31) and (4.5.76) yields

$$\begin{aligned} l_{22,22} &= kT(c_2 + 2\gamma), \\ l_{222,2} &= -(kT)^2(2\gamma + 3c_2), \\ l_{2222} &= 2(kT)^3(4\gamma + 3c_2). \end{aligned} \tag{4.5.77}$$

Here we have used the fact that $\varepsilon_2 = -1$ since the parameter p is time-odd.

The other elements of the matrices $l_{\alpha\beta,\gamma\delta}$, $l_{\alpha\beta\gamma,\delta}$, $l_{\alpha\beta\gamma\delta}$ are equal to zero. Since (4.5.75) does not contain the quadratic terms, all three-subscript coefficients $l_{...}$ are equal to zero in our example. Using (4.1.12), we easily find the two-subscript matrix $l_{\alpha\beta}$:

$$l_{22} = 2kTR, \quad l_{12} = l_{11} = 0. \tag{4.5.78}$$

Further, applying (4.3.35) and (4.5.77) gives

$$\begin{aligned} K_{2222} &= 2(kT)^3(4\gamma + 3c_2), \\ K_{222}(p) &= -(kT)^2(2\gamma + 3c_2)p/L. \end{aligned} \tag{4.5.79}$$

The other $K_{\alpha\beta\gamma\delta}$ and $K_{\alpha\beta\gamma}$ are equal to zero. Then according to (4.3.36, 37) we get

$$K_{22}(p) = 2kTR + \frac{1}{2}kT(c_2 + 2\gamma)(p|L)^2 - \frac{1}{2}(kT)^2(c_2 + 2\gamma)L^{-1},$$

$$K_{12} = K_{11} = 0,$$

$$K_2(Q, p) = -\frac{Q}{C} - R \frac{p}{L} - \frac{\gamma}{6} \left(\frac{p}{L} \right)^3 + \frac{kT\gamma}{2L^2} p, \tag{4.5.80}$$

$$K_1(Q, p) = p/L.$$

If, using the coefficients (4.5.79, 80), we write down the master equation

$$\dot{w}(Q, p) = L_1 w + L_2 w \tag{4.5.81}$$

(where L_1 is the operator of the linear approximation), then the resultant expression

$$\begin{aligned} L_2 w = & \frac{\gamma}{6L^3} \frac{\partial}{\partial p} [(p^3 - 3kTLp)w] + kT \frac{c_2 + 2\gamma}{4L^2} \frac{\partial^2}{\partial p^2} [(p^2 - kTL)w] \\ & + \frac{(kT)^2}{6L} (4\gamma + 3c_2) \frac{\partial^3(pw)}{\partial p^3} + \frac{(kT)^3}{12} (4\gamma + 3c_2) \frac{\partial^4 w}{\partial p^4} \end{aligned} \quad (4.5.82)$$

will be similar to the corresponding expression in (4.5.69). It is natural since the same nonlinear resistor has been taken in both examples. The difference is that in the preceding example the presence of the nonlinear resistor influenced the equation for time-even variable, and it now influences the equation for time-odd variable.

4.5.7 Nonlinear Friction in the Case of a Spherical Body Moving in a Homogeneous Isotropic Medium

Parallel with linear friction we will consider the nonlinear, namely, cubic part of the frictional force. In the isotropic medium we have the following formula for the vector frictional force:

$$f_{fr}(v) = \gamma v + \lambda v^2 v . \quad (4.5.83)$$

Terms quadratic in velocity vanish owing to the isotropy condition. Using (4.5.83), we have the vector phenomenological equation

$$m\dot{v} = -\gamma v - \lambda v^2 v . \quad (4.5.84)$$

Let us take the momentum vector components $p = mv$ as B_1, B_2, B_3 . Then from (4.5.84) we have the standard equation

$$\dot{p}_\alpha = -\gamma v_\alpha - \lambda v^2 v_\alpha \equiv \kappa_\alpha(v) \quad (4.5.85)$$

since $v_\alpha = x_\alpha$ are the forces conjugate to p_α .

Differentiating the right-hand side of (4.5.85) according to (4.1.6) gives

$$l_{\alpha,\beta} = -\gamma \delta_{\alpha\beta} , \quad (4.5.86a)$$

$$l_{\alpha,\beta\gamma\sigma} = -2\lambda(\delta_{\alpha\beta}\delta_{\gamma\sigma} + \delta_{\alpha\gamma}\delta_{\beta\sigma} + \delta_{\alpha\sigma}\delta_{\beta\gamma}) . \quad (4.5.86b)$$

Substituting (4.5.86) into (4.1.12, 28) and using

$$\kappa_{\alpha\beta}(v) = l_{\alpha\beta} + \frac{1}{2} l_{\alpha\beta,\gamma\sigma} v_\gamma v_\sigma , \quad (4.5.87)$$

we obtain

$$\kappa_{\alpha\beta}(v) = 2kT\gamma\delta_{\alpha\beta} + 2kT\lambda(v^2\delta_{\alpha\beta} + 2v_\alpha v_\beta) + \frac{1}{2}kTc_{\alpha\beta,\gamma\sigma}v_\gamma v_\sigma . \quad (4.5.88)$$

In the isotropic case the tensor $c_{\alpha\beta,\gamma\sigma}v_\gamma v_\sigma$ must be expressed only in terms of $\delta_{\rho\sigma}$ and vector v_ρ . Considering all the possible tensor combinations of $\delta_{\rho\sigma}$ and v_ρ (there are only two of them), we get

$$\frac{1}{2}c_{\alpha\beta,\gamma\sigma}v_\gamma v_\sigma = c_{||}v_\alpha v_\beta + c_\perp(v^2\delta_{\alpha\beta} - v_\alpha v_\beta) . \quad (4.5.89)$$

Here $c_{||}$ and c_{\perp} are independent dissipationally undeterminable parameters. We see that there are only two such parameters. From the physical point of view it is clear that the motion of the body chiefly influences the random force components parallel to its velocity. Therefore, in (4.5.89) the main contribution is given by the parameter $c_{||}$. The transverse parameter c_{\perp} must be much smaller than $c_{||}$ or even equal to zero.

The dissipationally undeterminable matrix

$$c_{\alpha\beta,\gamma\sigma} = (c_{||} - c_{\perp})(\delta_{\alpha\gamma}\delta_{\beta\sigma} + \delta_{\alpha\sigma}\delta_{\beta\gamma}) + 2c_{\perp}\delta_{\alpha\beta}\delta_{\gamma\sigma} \quad (4.5.90)$$

corresponds to (4.5.89). It is easy to verify that this matrix satisfies (4.1.27). As a consequence of (4.5.89), equation (4.5.88) assumes the form

$$\kappa_{\alpha\beta}(v) = 2kT\gamma\delta_{\alpha\beta} + kT(2\lambda + c_{\perp})v^2\delta_{\alpha\beta} + kT(4\lambda + c_{||} - c_{\perp})v_{\alpha}v_{\beta}. \quad (4.5.91)$$

Considering (4.5.86) and the form of the matrix $l_{\alpha\beta,\gamma\sigma}$ corresponding to (4.5.91), according to (4.3.36, 37) we find

$$\begin{aligned} K_{\alpha\beta}(p) &= [2kT\gamma + kTm^{-2}(2\lambda + c_{\perp})(p^2 - 3kTm)]\delta_{\alpha\beta} \\ &\quad + kTm^{-2}(4\lambda + c_{||} - c_{\perp})(p_{\alpha}p_{\beta} - kTm\delta_{\alpha\beta}), \\ K_{\alpha}(p) &= -\gamma m^{-1}p_{\alpha} - \lambda m^{-3}(p^2 - 5kTm)p_{\alpha}. \end{aligned} \quad (4.5.92)$$

Further, using (4.5.86, 90), according to (4.1.29, 31) and then from (4.3.35) we obtain

$$\begin{aligned} K_{\alpha\beta\gamma\sigma} &= 4(kT)^3(4\lambda + c_{||})(\delta_{\alpha\beta}\delta_{\gamma\sigma} + \delta_{\alpha\gamma}\delta_{\beta\sigma} + \delta_{\alpha\sigma}\delta_{\beta\gamma}), \\ K_{\alpha\beta\gamma}(p) &= -2(kT)^2m^{-1}(4\lambda + c_{||})(p_{\alpha}\delta_{\beta\gamma} + p_{\beta}\delta_{\alpha\gamma} + p_{\gamma}\delta_{\alpha\beta}). \end{aligned} \quad (4.5.93)$$

We now use the coefficients (4.5.92, 93) to write the master equation corresponding to this example:

$$\begin{aligned} \dot{w}(p) &= L_1 w + \lambda m^{-3} \frac{\partial}{\partial p_{\alpha}} [(p^2 - 5kTm)p_{\alpha}w] + 2^{-1}m^{-2}kT \\ &\quad \times \Delta_p \{(c'(p^2 - 3kTm) - c''kTm)w\} + 2^{-1}m^{-2}kTc'' \frac{\partial^2}{\partial p_{\alpha}\partial p_{\beta}} (p_{\alpha}p_{\beta}w) \\ &\quad + m^{-1}(kT)^2(4\lambda + c_{||})\Delta_p \frac{\partial}{\partial p_{\alpha}} (p_{\alpha}w) + 2^{-1}(kT)^3(4\lambda + c_{||})\Delta_p^2 w. \end{aligned} \quad (4.5.94)$$

Here

$$\begin{aligned} c' &= 2\lambda + c_{\perp}, \\ c'' &= 4\lambda + c_{||} - c_{\perp}, \\ \Delta_p &= \sum_{\alpha} \partial^2/\partial p_{\alpha}^2, \\ L_1 w &= m^{-1}\gamma \frac{\partial}{\partial p_{\alpha}} (p_{\alpha}w) + kT\gamma\Delta_p w. \end{aligned} \quad (4.5.95)$$

We note that in (4.5.94) the part of the kinetic operator conditioned by dissipative

nonlinearity remains the same if the body under study moves in an external mechanical potential $\Pi(\mathbf{r})$ (even if the force $f(\mathbf{r}) = -\operatorname{grad} \Pi(\mathbf{r})$ depends nonlinearly on \mathbf{r}). In this case the operator of the linear approximation will change and take the form

$$L_1 = -(p_\alpha/m_\alpha)\partial/\partial r_\alpha + (\partial/\partial p_\alpha)[\partial\Pi(\mathbf{r})/\partial r_\alpha + (\gamma/m)p_\alpha] + kT\gamma A_p. \quad (4.5.96)$$

Here w is a function of p and \mathbf{r} . Despite the fact that the process is now described by six variables, only two dissipationally undeterminable parameters appear here as in the previous example.

4.5.8 Nonlinear Electrical Conduction in an Isotropic Medium

Let us now consider the case of a continuum number of variables. Namely, we will deal with electromagnetic fields satisfying Maxwell's equations (4.4.92). Let the isotropy condition be fulfilled; hence,

$$\begin{aligned} B_k &= \mu H_k, \\ D_k &= \varepsilon_1 E_k + \varepsilon_3 E^2 E_k, \end{aligned} \quad (4.5.97)$$

i.e. cubic nonlinearity is assumed.

Assuming nonlinear conduction, in the isotropic case we will have

$$j_k = \sigma E_k + \lambda E^2 E_k \quad (4.5.98)$$

instead of (4.4.95). Substituting this equation into (4.4.92) gives

$$\dot{\mathbf{D}} = \operatorname{curl} \mathbf{H} - \sigma \mathbf{E} - \lambda \mathbf{E}^2 \mathbf{E} \equiv \kappa(\mathbf{H}, \mathbf{E}), \quad (4.5.99a)$$

$$\dot{\mathbf{B}} = -\operatorname{curl} \mathbf{E} \equiv \kappa'(\mathbf{H}, \mathbf{E}). \quad (4.5.99b)$$

These equations have the standard form since, as noted in Sect. 4.4.7, the variables E_k and H_k play the role of the thermodynamic forces conjugate to D_k and B_k , respectively. Equations (4.5.99) are a special case of (4.3.9).

The two-subscript coefficients $l_{\alpha\beta}$ corresponding to the linear terms on the right-hand side of (4.5.99) have been found in Sect. 4.4.7. Considering the nonlinear terms in (4.5.99a), we find the four-subscript coefficients

$$l_{jklm}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = -2\lambda I_{jklm}\delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \quad (j, k, l, m = 1, 2, 3), \quad (4.5.100)$$

where

$$\begin{aligned} l_{jklm} &= \delta_{jk}\delta_{lm} + \delta_{jl}\delta_{km} + \delta_{jm}\delta_{kl}, \\ \delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) &= \delta(\mathbf{r}_{12})\delta(\mathbf{r}_{23})\delta(\mathbf{r}_{34}). \end{aligned} \quad (4.5.101)$$

The other l_{jklm} ($1 \leq j, k, l, m \leq 6$) are equal to zero. We see that (4.5.100) are analogous to (4.5.86b). Using the condition of isotropy, we take the dissipationally undeterminable matrix in the form

$$c_{jk,lm}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_3, \mathbf{r}_4) = 2(c_1 \delta_{jk}\delta_{lm} + c_2 I_{jklm})\delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4). \quad (4.5.102)$$

For the other subscripts we have $c_{jk,lm} = 0$. In (4.5.102) the multiplier $\delta(\mathbf{r}_1, \dots, \mathbf{r}_4)$

is placed in analogy with (4.5.100). We use “the continuation principle”: the properties of the dissipationally undeterminable matrix must imitate the general properties of the matrix $l_{\alpha, \beta, \gamma, \delta}$.

Using (4.5.100, 102), according to (4.1.28, 29, 31) and (4.3.35, 37), we get

$$K_{jklm}(\mathbf{r}_1, \dots, \mathbf{r}_4) = 4(kT)^3(4\lambda + 3c_2 + c_1)I_{jklm}\delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4), \quad (4.5.103a)$$

$$\begin{aligned} K_{jkl}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{E}) = & -2(kT)^2(4\lambda + 3c_2 + c_1) \\ & \times (E_j\delta_{kl} + E_k\delta_{jl} + E_l\delta_{jk})\delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \end{aligned} \quad (4.5.103b)$$

$$\begin{aligned} K_{jk}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{E}) = & kT[2\sigma\delta_{jk} + (2\lambda + c_1 + c_2)E^2\delta_{jk} + 2(2\lambda + c_2)E_jE_k]\delta(\mathbf{r}_{12}), \\ j, k, l, m = 1, 2, 3. \end{aligned} \quad (4.5.103c)$$

The small terms whose relative magnitude is of order kT are not considered here.

The coefficients of the continuum master equation are thus determined. It is essential that (4.5.99, 103) have the same form both for the linear dependences of \mathbf{D} and \mathbf{B} on \mathbf{E} and \mathbf{H} , respectively, and for the nonlinear ones. Naturally, for the nonlinear dependence the form of the master equation coefficients as functionals of \mathbf{D} and \mathbf{B} will be different.

Thus, although the variables are continuous, we have only two dissipationally undeterminable parameters in the isotropic case (spatial dispersion is assumed to be absent as in Sect. 4.4.7).

In Sect. 4.5 various specific master equations have been obtained in the case in which nonlinear dissipation is taken into account. Solving these equations, we can find the various equilibrium and nonequilibrium correlators for fluctuation–dissipation processes including non-Gaussian characteristics of these processes. It should be noted that the solution of these equations is facilitated by the fact that the kinetic operator terms conditioned by the dissipative nonlinearity are relatively small. Therefore, small parameter methods can be applied for solving the master equation.

In conclusion we note that the condition of nonnegativity of the various probability densities can be violated for the particular master equations (4.5.21, 69) and for the others that contain terms with the third and fourth derivatives. However, since these additional terms are absolutely and relatively small (they are of order $(kT)^2$ and $(kT)^3$, respectively), the violation of nonnegativity is negligible.

4.6 *H*-Theorems of Markov Nonequilibrium Thermodynamics

4.6.1 *H*-Theorems of Linear Theory

Let us take the third formulation of the second law of thermodynamics (2.2.24), according to which the inequality $dF(a)/dt \leq 0$ is valid if all $da_\alpha = 0$. For a thermally isolated system one should take the inequality $dS/dt \geq 0$. If the conditional free energy or the conditional entropy is used, the second law of thermodynamics is expressed by (2.2.101) or (2.2.102). In order to be definite let us consider

the free-energy version. Using (3.1.38), which is analogous to (2.2.97), we have

$$\frac{dF(A)}{dt} = \frac{\partial F(A)}{\partial A_\alpha} \frac{dA_\alpha}{dt} = x_\alpha \dot{A}_\alpha. \quad (4.6.1)$$

Here we have assumed that $F(A)$ does not explicitly depend on t , i.e. $\partial F/\partial t = 0$. In the linear approximation the formula $\dot{A}_\alpha = l_{\alpha,\beta} x_\beta$ following from (4.3.9, 17) is valid. Owing to this, the derivative (4.6.1) can be written as

$$\dot{F}(A) = l_{\alpha,\beta} x_\alpha x_\beta. \quad (4.6.2)$$

Hence, we have

$$\dot{F}(A) = \frac{1}{2}(l_{\alpha,\beta} + l_{\beta,\alpha})x_\alpha x_\beta. \quad (4.6.3)$$

Using (4.1.12), we get from (4.6.3)

$$\dot{F}(A) = -(2kT)^{-1} l_{\alpha\beta} x_\alpha x_\beta = -(2kT)^{-1} \kappa_{\alpha\beta}(0) x_\alpha x_\beta. \quad (4.6.4)$$

Here (4.1.6) at $m = 2, n = 0$ is used. According to (3.1.76), (4.6.4) assumes the form

$$\begin{aligned} \dot{F}(A) &= -(2kT)^{-1} \lim_{\tau \rightarrow 0} [\tau^{-1} \langle \Delta B_\alpha \Delta B_\beta \rangle_0 x_\alpha x_\beta] \\ &= -(2kT)^{-1} \lim_{\tau \rightarrow 0} [\tau^{-1} \langle (x_\alpha \Delta B_\alpha)^2 \rangle_0], \end{aligned} \quad (4.6.5)$$

where

$$\langle \Delta B_\alpha \Delta B_\beta \rangle_0 = [\langle \Delta B_\alpha \Delta B_\beta \rangle_B]_{x=0} \quad (4.6.6)$$

are the equilibrium means. In (4.6.5) the nonnegative quantity $(\sum_\alpha x_\alpha \Delta B_\alpha)^2$ is averaged. Its mean value $\langle (x_\alpha \Delta B_\alpha)^2 \rangle_0$ must be nonnegative. The limit of the nonnegative quantity is nonnegative. This proves the inequality $\dot{F}(A) \leq 0$. It should be noted that in the nontrivial cases when the matrix $K_{\alpha\beta}$ is nondegenerate, this inequality is valid with the sign $<$, as one can see from (4.6.4), i.e. from equation

$$\dot{F} = -(2kT)^{-1} x_\alpha x_\beta \int K_{\alpha\beta} w_{\text{eq}}(B) dB = -(2kT)^{-1} x_\alpha x_\beta K_{\alpha\beta}$$

(so that $\dot{F} \neq 0$) and from $\dot{F} \leq 0$. Inequality $\dot{S} \geq 0$ can be proved in an analogous way.

Prigogine's theorem bears a close relationship to the H -theorem of the linear theory. We will consider Prigogine's theorem in the free-energy version though it was originally proved in the entropy version.

Theorem. *If the internal parameters A_α have the same time parity, the production of free energy*

$$P = \dot{F} \quad (4.6.7)$$

does not decrease in the framework of the linear theory: $\dot{P} \geq 0$. In the entropy version $P = -\dot{S}$.

Proof. Differentiating (4.6.2) with respect to time and considering (3.1.38) gives

$$\dot{P} = \frac{d}{dt} l_{\alpha, \beta} \frac{\partial F}{\partial A_\alpha} \frac{\partial F}{\partial A_\beta} = (l_{\alpha, \beta} + l_{\beta, \alpha}) \frac{\partial F}{\partial A_\alpha} \frac{\partial^2 F}{\partial A_\beta \partial A_\gamma} \dot{A}_\gamma . \quad (4.6.8)$$

When all parameters A_α have the same parity, the Onsager relation (4.1.14) is valid. Therefore, (4.6.8) yields

$$\dot{P} = 2 \frac{\partial^2 F}{\partial A_\beta \partial A_\gamma} l_{\beta, \alpha} \frac{\partial F}{\partial A_\alpha} \dot{A}_\gamma . \quad (4.6.9)$$

Using the relation $\dot{A}_\gamma = l_{\gamma, \delta} x_\delta$ once more, we arrive at

$$\dot{P} = 2 \frac{\partial^2 F(A)}{\partial A_\beta \partial A_\gamma} l_{\beta, \alpha} \frac{\partial F}{\partial A_\alpha} l_{\gamma, \delta} \frac{\partial F}{\partial A_\delta} . \quad (4.6.10)$$

Owing to the stability of the equilibrium point $A = A_{\text{eq}}$ the matrix $\partial^2 F(A)/\partial A_\beta \partial A_\gamma$ is positive definite at this point. In the linear approximation we can take $[\partial^2 F/\partial A_\beta \partial A_\gamma]_{A=A_{\text{eq}}}$ instead of $\partial^2 F(A)/\partial A_\beta \partial A_\gamma$; the matrix in (4.6.10) is, therefore, positive definite. But due to positive definiteness we have

$$\frac{\partial^2 F(A)}{\partial A_\beta \partial A_\gamma} u_\beta u_\gamma \geq 0 \quad (4.6.11)$$

for any u_β including $u_\beta = l_{\beta, \alpha} x_\alpha$. Consequently, the expression on the right-hand side of (4.6.10) is nonnegative; this proves the theorem. \square

The inequality $\ddot{S} \leq 0$ of the entropy version can be proved analogously.

Note that Prigogine's theorem, which is less general than the H -theorem (since it demands that the parameters are of the same parity), is at the same time a stronger statement than the H -theorem. In fact, let us show that the H -theorem follows from it. If P does not decrease in the process of the relaxation to the equilibrium state, then in the equilibrium state P is not less than what it is in the nonequilibrium state:

$$P_{\text{eq}} \geq P . \quad (4.6.12)$$

But in the equilibrium state the parameters do not change and, hence, the production of free energy is equal to zero: $P_{\text{eq}} = 0$. Therefore, from (4.6.12) we obtain $P \leq 0$, i.e. the H -theorem statement.

4.6.2 The Second Law of Thermodynamics in the Linear Approximation: An Example

From the large number of examples we consider only one, namely, the case of the chemical reaction, which was discussed in Sect. 4.4.8. In this example the molar densities $c_1(\mathbf{r})$ and $c_2(\mathbf{r})$ play the role of internal parameters A_α , $\alpha = (i, \mathbf{r})$, and (4.6.1) reads

$$\dot{F} = \sum_{i=1}^2 \int x_i(\mathbf{r}) \dot{c}_i(\mathbf{r}) d\mathbf{r} . \quad (4.6.13)$$

Substituting (4.4.110) into (4.6.13) and considering (4.4.111), we obtain

$$\dot{F} = -\frac{k'_1}{RT} \int (x_1 - 2x_2)^2 d\mathbf{r} + \frac{1}{RT} \int (D'_1 x_1 \Delta x_1 + D'_2 x_2 \Delta x_2) d\mathbf{r}. \quad (4.6.14)$$

Using Green's formula

$$\int_V [\psi \Delta \varphi + \nabla \psi \cdot \nabla \varphi] d\mathbf{r} = \int_S \psi (\Delta \varphi)_n dS, \quad (4.6.15)$$

we can reduce the last expression to the form

$$\dot{F} = -\frac{k'_1}{RT} \int (x_1 - 2x_2)^2 d\mathbf{r} - \frac{1}{RT} \int [D'_1 (\nabla x_1)^2 + D'_2 (\nabla x_2)^2] d\mathbf{r}. \quad (4.6.16)$$

Here the surface integral has been omitted since we assume that there is no influx of the substance from the surrounding medium [$(\nabla x_1)_n$ and $(\nabla x_2)_n$ are equal to zero on the boundary].

The constants k'_1 , D'_1 and D'_2 are nonnegative; therefore, (2.2.102) holds in the case of (4.6.16). If at least one of the quantities $k'_1(x_1 - 2x_2)$, $D'_1 \nabla x_1$ and $D'_2 \nabla x_2$ is not equal to zero, the inequality (2.2.102) is valid with the sign $<$.

It is easy to verify the validity of the inequality $\ddot{F} \geq 0$ for the present example.

4.6.3 The H -Theorem of the Nonlinear Theory

Comparing the expansion (3.1.41) with (3.1.80), we find the formula connecting the kinetic potential images $R(y, x)$ and $R_f(y, x)$:

$$R(y, x) = y_\alpha \kappa_\alpha(x) + R_f(y, x). \quad (4.6.17)$$

Substituting (4.6.17) into the generating equation (3.1.36) resulting from the stationary equation (3.1.12), we get

$$x_\alpha \kappa_\alpha(x) = -R_f(x, x). \quad (4.6.18)$$

Here R_f is nonnegative according to (3.1.79). Therefore, from (4.6.18) we have

$$x_\alpha \kappa_\alpha(x) \leq 0. \quad (4.6.19)$$

But by virtue of (4.3.9), $\kappa_\alpha(x)$ can be treated as \dot{A}_α , and the expression on the left-hand side of (4.6.19) coincides with the derivative (4.6.1). Consequently, from (4.6.19) we obtain $\dot{F} \leq 0$. Hence, the theorem is proved. It is essential that by virtue of (4.6.18) and (3.1.76, 80) the derivative \dot{F} , which can be written as

$$\dot{F} = -kT \lim_{\tau \rightarrow 0} \tau^{-1} \langle \exp(\beta x \Delta B) - 1 - \beta x \Delta B \rangle_x, \quad (4.6.20)$$

is strictly negative (because the function $e^z - 1 - z$ is positive for $z \neq 0$) with the exception of the trivial cases when $\dot{A} = 0$ or the process $B_\alpha(t)$ is nonfluctuational.

Example. Let us take the same example as that considered in Sect. 4.6.2, but we now substitute the nonlinear equations (4.4.108) into (4.6.13). Using Green's

formula (4.6.15) again, we obtain the equation

$$\begin{aligned}\dot{F} = & -RTk'_1 \int f[(x_1 - 2x_2)/RT] \exp(2x_2/RT) dr \\ & - (RT)^{-1} \int [D'_1 \exp(x_1/RT)(\text{grad } x_1)^2 \\ & + D'_2 \exp(x_2/RT)(\text{grad } x_2)^2] dr ,\end{aligned}\quad (4.6.21)$$

which is more precise than (4.6.16). Here

$$f(z) = z(e^z - 1) . \quad (4.6.22)$$

Since (4.6.22) is nonnegative, the inequality $\dot{F} \leq 0$ follows from (4.6.21).

4.6.4 Can Prigogine's Theorem Be Generalized to the Nonlinear Case?

We have seen that the H -theorem of the linear theory is directly generalized to the nonlinear case. This cannot be said about Prigogine's theorem, which cannot be extended beyond the framework of the linear theory.

In order to prove a statement, in the nonlinear case the following quantity

$$\frac{d_x P}{dt} = \frac{d_x(x_\alpha J_\alpha)}{dt} \equiv J_\alpha \frac{dx_\alpha}{dt} \quad (4.6.23)$$

is sometimes introduced, where $J_\alpha = \dot{A}_\alpha$.

It is easy to prove that

$$d_x P/dt \geq 0 \quad (4.6.24)$$

if $F(A)$ is convex for all A .

In fact, by virtue of (4.6.23) and (3.1.38) we have

$$\frac{d_x P}{dt} = \dot{A}_\alpha \frac{d}{dt} \left(\frac{\partial F(A)}{\partial A_\alpha} \right) = \frac{\partial^2 F(A)}{\partial A_\alpha \partial A_\beta} \dot{A}_\alpha \dot{A}_\beta . \quad (4.6.25)$$

The matrix $\partial^2 F(A)/\partial A_\alpha \partial A_\beta$ is nonnegative definite owing to the above-mentioned convexity of $F(A)$. Therefore, the expression on the right-hand side of (4.6.25) is nonnegative. This proves (4.6.24).

It should be noted that the inequality (4.6.24) is of little importance for the following reasons:

1. While Prigogine's theorem (Sect. 4.6.1) is a consequence of the Onsager relations, i.e. of the time reversibility, and the H -theorem of Sect. 4.6.3 is a consequence of the dynamic equilibrium, the statement (4.6.24) is a trivial consequence of the definition (4.6.23) and of the convexity of $F(A)$.

2. In the general case the specific differential $d_x P$ is not the total one, so that (4.6.24) does not imply the increase of any function.

3. The function $F(A)$ is convex at the equilibrium point A_{eq} and in its neighbourhood, but it is not required to be convex everywhere. In particular, it is not convex everywhere when there are phase transitions and bistabilities. For this

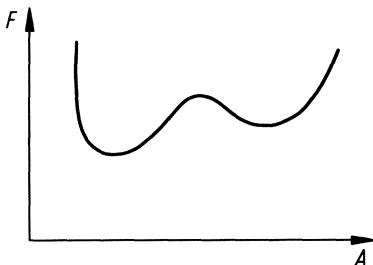


Fig. 4.7. Behaviour of the free energy in the case of metastability

case the behaviour of $F(A)$ is shown qualitatively in Fig. 4.7. Therefore, equation (4.6.24) is not always valid.

The above criticism also applies to cases where an inequality of the type (4.6.24) is derived for open systems with nonequilibrium stationary states.

4.7 Notes on References to Chapter 4

In Sects. 1.2, 3 we have already referred to the works in which the linear and nonlinear Markov nonequilibrium thermodynamics relations were first obtained. The generating equation in a form similar to (4.1.40) was derived in [4.5] for the case of time-even parameters. For more general case this sort of the generating equation was obtained in [4.6]. The consequences of this generating equation were considered in the same work.

The problem of finding the coefficient functions and, thereby, the problem of constructing the master equation (the Fokker–Planck equation) was first solved in the linear approximation for Brownian motion by *Einstein* [4.3]. In the nonlinear approximations this problem was considered in [4.7]. In [4.8] the reconstruction of the master equation form, when the phenomenological equation was known, was made in the linear–cubic approximation for one special example. This master equation was solved by an approximate method in the same work.

Examples of the application of reciprocal relations can be found in many manuals, for instance, in [4.9–11]. Some examples of the application of linear FDRs can be found in [4.12–15].

For various examples the validity of the linear H -theorems was shown in [4.10, 16]. Prigogine's theorem (its entropy version) was also proved in [4.17]. In [4.6] the nonlinear H -theorem was first proved by a method more complicated than necessary. In the present book a new simple proof has been given.

5. Fluctuation–Dissipation Relations of Non-Markov Theory

This chapter is central for the subject matter of the book. General linear, quadratic and cubic fluctuation–dissipation relations (FDRs) of nonequilibrium thermodynamics are derived here. These relations are not restricted by the condition of the Markov properties of the processes in question.

There are FDRs of the first, second and third kinds. Relations of the first kind are direct generalizations of the Markov relations to the non-Markov case. The reciprocal relation for the linear admittance and the ordinary fluctuation–dissipation theorem are the linear relations of the second kind. The nonlinear FDRs of the second kind, which are concerned with nonlinear admittances, correlators of internal parameters and other functions, are also considered.

The linear and nonlinear relations of the third kind characterize the random forces arising in the dissipative elements of the system and causing fluctuations of internal parameters. The FDRs of the third kind relate the impedances (linear and nonlinear) to those characteristics of random forces that depend neither on the fluctuations arising in other elements of the system, nor on their temperature. These characteristics are also independent of how and where the element being considered is connected to the system. The reciprocal relation for the linear impedance and the Nyquist formula are linear relations of the third kind.

It is remarkable that the FDRs of the various kinds have analogous forms.

5.1 Non-Markov Phenomenological Relaxation Equations and FDRs of the First Kind

5.1.1 Relaxation Equations with After-effects

When the process $\{B_\alpha(t)\}$ is non-Markovian, i.e. the process exhibits after-effects, the simple phenomenological equations (4.3.1) are invalid. One should instead take

$$\dot{A}_\alpha = - \chi_\alpha[A(\cdot)] , \quad \alpha = 1, \dots, r , \quad (5.1.1)$$

where after-effects are taken into account. Here $\chi_\alpha[A(\cdot)]$ are functionals of $A(t)$ such that the values $A(t_2)$ influence $\dot{A}(t_1)$ only for $t_2 \leq t_1$.

If the right-hand side of (5.1.1) is expressed in terms of the forces (3.1.38) corresponding, say, to the energy version, we obtain the standard form of relaxation equations:

$$\dot{A}_\alpha = - \Psi_\alpha[x(\cdot)] . \quad (5.1.2)$$

These equations are generalizations of (4.3.9) to the case with after-effects. Expanding $\Psi_\alpha[x(\cdot)]$ in a Taylor series in $x(t)$ gives

$$\begin{aligned}\dot{A}_{\alpha_1}(t_1) &= - \int \Phi_{\alpha_1 \alpha_2}(t_1, t_2) x_{\alpha_2}(t_2) dt_2 \\ &\quad - \frac{1}{2} \int \Phi_{\alpha_1, \alpha_2 \alpha_3}(t_1, t_2, t_3) x_{\alpha_2}(t_2) x_{\alpha_3}(t_3) dt_2 dt_3 + \dots,\end{aligned}\quad (5.1.3)$$

where the conditions $\Phi_\alpha[0] = 0$ have been used.

Replacing the pairs $(\alpha_1, t_1), (\alpha_2, t_2), \dots$ by subscripts $1, 2, \dots$, respectively, we can write (5.1.3) in the shorter form

$$\dot{A}_1 = -\Phi_{1,2}x_2 - \frac{1}{2}\Phi_{1,23}x_2x_3 + \dots. \quad (5.1.4)$$

Here summation and/or integration over repeated subscripts is understood.

In certain examples, the subscript α can include a continuous variable, e.g. one can take j, \mathbf{r} as α , where \mathbf{r} is the radius vector. Then, 1 means j_1, \mathbf{r}_1, t_1 , etc. The part of the components of the many-component Markov process can be taken as an example of the non-Markov process. Suppose that the set of variables $(A_1, \dots, A_r, C_{r+1}, \dots, C_{m+1})$ constitute the Markov process. We assume that the subscripts i, j, k run through the values $1, \dots, r+m$, the subscripts α, β, γ run through the values $1, \dots, r$ and that the subscripts $\rho, \sigma, \tau, \pi, \varphi$ run through the values $r+1, \dots, r+m$. Then we have $\{B_i\} = \{A_\alpha, C_\rho\}$. Let us write (4.3.9) for the Markov process $\{B_i(t)\}$. With the above notation these equations can be written as

$$\begin{aligned}\dot{A}_\alpha &= \kappa_\alpha(x) \\ &= l_{\alpha, \beta}x_\beta + l_{\alpha, \sigma}x_\sigma + \frac{1}{2}l_{\alpha, \beta\gamma}x_\beta x_\gamma + l_{\alpha, \beta\sigma}x_\beta x_\sigma + \frac{1}{2}l_{\alpha, \sigma\tau}x_\sigma x_\tau + \dots,\end{aligned}\quad (5.1.5a)$$

$$\begin{aligned}\dot{C}_\rho &= \kappa_\rho(x) \\ &= l_{\rho, \beta}x_\beta + l_{\rho, \sigma}x_\sigma + \frac{1}{2}l_{\rho, \beta\gamma}x_\beta x_\gamma + l_{\rho, \beta\sigma}x_\beta x_\sigma + \frac{1}{2}l_{\rho, \sigma\tau}x_\sigma x_\tau + \dots.\end{aligned}\quad (5.1.5b)$$

Here the notation of (4.1.6) is used.

By using (5.1.5b), one can in principle find $C_\rho(t)$ as functionals of $A_\alpha(\cdot)$:

$$C_\rho(t) = F_\rho(t, A_\alpha(\tau)) \equiv F_\rho[A(\tau)]. \quad (5.1.6)$$

Substituting $x_\sigma = x_\sigma(A_\rho) = x_\sigma(F_\rho[A])$ into (5.1.5a), we can obtain equation (5.1.1) with after-effects for A_1, \dots, A_r .

5.1.2 Linear Approximation: Reciprocal Relations

In the linear approximation we have

$$\dot{A}_\alpha = l_{\alpha, \beta}x_\beta + l_{\alpha, \sigma}x_\sigma, \quad \dot{C}_\rho = l_{\rho, \beta}x_\beta + l_{\rho, \sigma}x_\sigma. \quad (5.1.7)$$

Here we can assume that x_i depend linearly on A_i :

$$x_i(B_j) = u_{ij}B_j, \quad (5.1.8a)$$

$$x_\alpha = u_{\alpha\beta}A_\beta, \quad (5.1.8b)$$

$$x_\rho = u_{\rho\sigma}C_\sigma. \quad (5.1.8c)$$

The cross-coefficients $u_{\alpha\sigma}$ and $u_{\rho\beta}$ are set equal to zero. This corresponds to the assumption that the components A_α are statistically independent of C_ρ in the framework of the one-time equilibrium probability density $w_{\text{eq}}(B)$. On substituting (5.1.8) into (5.1.7) we get

$$\dot{A} = -\hat{D}_1 A - \hat{D}_{12} C, \quad (5.1.9a)$$

$$\dot{C} = -\hat{D}_{21} A - \hat{D}_2 C, \quad (5.1.9b)$$

where

$$A = \begin{pmatrix} A_1 \\ \vdots \\ A_r \end{pmatrix}, \quad C = \begin{pmatrix} A_{r+1} \\ \vdots \\ A_{r+m} \end{pmatrix}, \quad \begin{aligned} \hat{D}_1 &= -\|l_{\alpha,\beta} u_{\beta\gamma}\|, \\ \hat{D}_2 &= -\|l_{\rho,\sigma} u_{\sigma\tau}\|, \\ \hat{D}_{12} &= -\|l_{\alpha,\sigma} u_{\sigma\tau}\|, \dots \end{aligned} \quad (5.1.10)$$

Solving (5.1.9b), we can find the dependence (5.1.6) corresponding to the linear approximation, namely

$$C(t) = - \int_{-\infty}^t \exp[-\hat{D}_2(t-t')] \hat{D}_{21} A(t') dt'. \quad (5.1.11)$$

Substitution of (5.1.11) into (5.1.9a) yields

$$\dot{A} = -\hat{D}_1 A + \hat{D}_{12} \int_{-\infty}^t \exp[-\hat{D}_2(t-t')] \hat{D}_{21} A(t') dt'. \quad (5.1.12)$$

Using the equations $\hat{D}_1 = -\|l_{\alpha,\beta} u_{\beta\gamma}\|$, $\hat{D}_{21} = -\|l_{\rho,\beta} u_{\beta\gamma}\|$ and (5.1.8b), we can write (5.1.12) as

$$\dot{A}_\alpha(t) = - \int \Phi_{\alpha,\beta}(t-t') x_\beta(t') dt', \quad (5.1.13)$$

where

$$\|\Phi_{\alpha,\beta}(t-t')\| = \begin{cases} -\hat{L}_1 \delta(t-t') + \hat{D}_{12} \exp[-\hat{D}_2(t-t')] \hat{L}_{21} & \text{for } t \geq t', \\ 0 & \text{for } t' > t, \end{cases} \quad (5.1.14)$$

$$\hat{L}_1 = \|l_{\alpha,\beta}\|, \quad \hat{L}_{21} = \|l_{\rho,\beta}\|.$$

The functions (5.1.14) are defined such that the right-hand side of (5.1.13) coincides with the linear term in (5.1.3).

Let us prove that the matrix (5.1.14) satisfies the reciprocal relations that are generalizations of the Onsager–Casimir relations:

$$\Phi_{\alpha,\beta}(t-t') = \varepsilon_\alpha \varepsilon_\beta \Phi_{\beta,\alpha}(t-t'). \quad (5.1.15)$$

Here the time difference $t-t'$ is arbitrary.

Using (5.1.10), which determines \hat{D}_{12} , \hat{D}_2 , we can write the matrix (5.1.14) in the form

$$\Phi_{\alpha,\beta}(s) = -l_{\alpha,\beta} \delta(s) - l_{\alpha,\sigma} u_{\sigma\tau} [\exp(\hat{L}_2 \hat{U}_2 s)]_{\tau\rho} l_{\rho,\beta}, \quad (5.1.16)$$

where $\hat{L}_2 = \|l_{\rho,\sigma}\|$, $\hat{U}_2 = \|u_{\rho\sigma}\|$ and $s = t-t' > 0$.

By virtue of (4.1.13) the term $l_{\alpha,\beta}\delta(s)$ satisfies a relation of the type (5.1.15). Therefore, for proving (5.1.15) it remains to prove that

$$l_{\alpha,\sigma}u_{\sigma\tau}[\exp(\hat{L}_2\hat{U}_2s)]_{\tau\rho}l_{\rho,\beta} = \varepsilon_\beta l_{\beta,\rho}u_{\rho\tau}[\exp(\hat{L}_2\hat{U}_2s)]_{\tau\alpha}l_{\sigma,\alpha}\varepsilon_\alpha. \quad (5.1.17)$$

Using the Onsager–Casimir relations (4.1.13) once again, we arrive at

$$\varepsilon_\beta l_{\beta,\rho} = l_{\rho,\beta}\varepsilon_\rho, \quad l_{\sigma,\alpha}\varepsilon_\alpha = \varepsilon_\sigma l_{\alpha,\sigma}. \quad (5.1.18)$$

Therefore for proving (5.1.17) it is sufficient to show that

$$\varepsilon_\rho(\hat{U}_2\exp(\hat{L}_2\hat{U}_2))_{\rho\sigma}\varepsilon_\sigma = (\hat{U}_2\exp(\hat{L}_2\hat{U}_2))_{\sigma\rho}. \quad (5.1.19)$$

The one-time equilibrium probability density of variables $B = (A, C)$ must satisfy the relation $W_{\text{eq}}(\varepsilon B) = W_{\text{eq}}(B)$, from which we have

$$\varepsilon_\rho u_{\rho\sigma} = u_{\rho\tau}\varepsilon_\tau \quad (5.1.20a)$$

or in matrix form

$$\varepsilon\hat{U}_2 = \hat{U}_2\varepsilon \quad (\hat{U}^\text{T} = \hat{U}). \quad (5.1.20b)$$

The validity of (5.1.19) follows from (5.1.20) and from the reciprocal relations $\varepsilon_\rho\varepsilon_\sigma l_{\rho,\sigma} = l_{\sigma,\rho}$; see (4.1.13). One can verify this statement by expanding the exponent in (5.1.19) in a series.

The relations

$$\varphi_{\alpha,\beta}(\omega) = \varepsilon_\alpha\varepsilon_\beta\varphi_{\beta,\alpha}(\omega) \quad (5.1.21)$$

which are written in the spectral representation as

$$\varphi_{\alpha,\beta}(\omega) = \int \exp(-i\omega s)\Phi_{\alpha,\beta}(s)ds \quad (5.1.22)$$

are equivalent to (5.1.15). We now introduce the operation of time conjugation denoted by the superscript “t.c.”. This operation consists in a change in the sign of time and in multiplication by time signatures ε_α :

$$\Phi_{\alpha_1,\alpha_2}(t_1 - t_2)^{\text{t.c.}} = \varepsilon_{\alpha_1}\varepsilon_{\alpha_2}\Phi_{\alpha_1,\alpha_2}(-t_1 + t_2). \quad (5.1.23)$$

Combining (5.1.15) with (5.1.23) yields

$$\Phi_{\alpha_1,\alpha_2}(t_1 - t_2)^{\text{t.c.}} = \Phi_{\alpha_2,\alpha_1}(t_2 - t_1). \quad (5.1.24)$$

Using the abbreviations employed in (5.1.4), we can write (5.1.24) in the shorter form

$$\Phi_{1,2}^{\text{t.c.}} = \Phi_{2,1}. \quad (5.1.25)$$

The last equation is valid not only in the time representation, but also in the spectral one. In other words, if we introduce the function

$$\Phi_{\alpha,\beta}(\omega_1, \omega_2) = (2\pi)^{-1} \int \exp(-i\omega_1 t_1 - i\omega_2 t_2)\Phi_{\alpha,\beta}(t_1, t_2)dt_1 dt_2 \quad (5.1.26)$$

(the factor in front of the integral is so chosen that the transformation is unitary), we have from (5.1.24)

$$\Phi_{\alpha,\beta}(\omega_1, \omega_2)^{t.c.} = \Phi_{\beta,\alpha}(\omega_2, \omega_1) , \quad (5.1.27)$$

where

$$\Phi_{\alpha,\beta}(\omega_1, \omega_2)^{t.c.} = \varepsilon_\alpha \varepsilon_\beta \Phi_{\alpha,\beta}(-\omega_1, -\omega_2) . \quad (5.1.28)$$

Replacing the pairs $(\alpha_1, \omega_1), (\alpha_2, \omega_2), \dots$ by subscripts $1, 2, \dots$, respectively, (5.1.27) can be written in the compact form (5.1.25). Consequently, (5.1.25) is invariant under a change of representation (the word “representation” here has the same meaning as in quantum theory).

In the stationary case, when $\Phi_{\alpha,\beta}(t_1, t_2)$ depends only on the time difference $t_{12} = t_1 - t_2$, the spectrum (5.1.26) is proportional to the δ -function:

$$\Phi_{\alpha,\beta}(\omega_1, \omega_2) = \varphi_{\alpha,\beta}(\omega_1) \delta(\omega_1 + \omega_2) , \quad (5.1.29)$$

where $\varphi_{\alpha,\beta}(\omega_1)$ is the function defined in (5.1.22). Therefore, (5.1.27) is equivalent to (5.1.21).

5.1.3 Linear FDR of the First Kind

Now we shall treat $[A(t), C(t)]$ as process undergoing fluctuations. The random functions will be denoted by the same letters as those that denote the mean values in (5.1.9). The Langevin equations

$$\dot{A} = -\hat{D}_1 A - \hat{D}_{12} C + \xi , \quad (5.1.30a)$$

$$\dot{C} = -\hat{D}_{21} A - \hat{D}_2 C + \eta , \quad (5.1.30b)$$

correspond to (5.1.9). According to (4.1.12), the random functions ξ, η have zero means and the correlators

$$\begin{aligned} \langle \xi_\alpha(t_1) \xi_\beta(t_2) \rangle &= -kT(l_{\alpha,\beta} + l_{\beta,\alpha}) \delta(t_{12}) , \\ \langle \xi_\alpha(t_1) \xi_\sigma(t_2) \rangle &= -kT(l_{\alpha,\sigma} + l_{\sigma,\alpha}) \delta(t_{12}) , \\ \langle \xi_\rho(t_1) \xi_\sigma(t_2) \rangle &= -kT(l_{\rho,\sigma} + l_{\sigma,\rho}) \delta(t_{12}) , \end{aligned} \quad (5.1.31)$$

or in matrix form

$$\langle \xi(t_1) \xi^T(t_2) \rangle = -kT(\hat{L}_1 + \hat{L}_1^T) \delta(t_{12}) , \quad (5.1.32a)$$

$$\langle \xi(t_1) \eta^T(t_2) \rangle = -kT(\hat{L}_{12} + \hat{L}_{21}^T) \delta(t_{12}) , \quad (5.1.32b)$$

$$\langle \eta(t_1) \eta^T(t_2) \rangle = -kT(\hat{L}_2 + \hat{L}_2^T) \delta(t_{12}) . \quad (5.1.32c)$$

Here the superscript T means the transposition of the matrix; ξ and η are column matrices, and ξ^T and η^T are row matrices. Integration of (5.1.30b) gives

$$C(t) = - \int_{-\infty}^t \exp[-\hat{D}_2(t-t')] \hat{D}_{21} A(t') dt' + \tilde{\eta}(t) , \quad (5.1.33)$$

where

$$\tilde{\eta}(t) = \int_{-\infty}^t \exp[-\hat{D}_2(t-t')] \eta(t') dt'. \quad (5.1.34)$$

By virtue of (5.1.33, 34) the one-time equilibrium correlator $\langle C_\rho, C_\sigma \rangle_0$ is given by

$$\begin{aligned} \langle C(t), C^\text{T}(t) \rangle_{\text{eq}} &= \langle \tilde{\eta}(t) \tilde{\eta}^\text{T}(t) \rangle \\ &= -kT \int_{-\infty}^t \exp[-\hat{D}_2(t-t')] (\hat{L}_2 + \hat{L}_2^\text{T}) \\ &\quad \times \exp[-\hat{D}_2^\text{T}(t-t')] dt', \end{aligned} \quad (5.1.35)$$

where (5.1.32c) has been used.

The linear approximation corresponds to the Gaussian equilibrium probability density

$$\begin{aligned} \tilde{w}_{\text{eq}}(A, C) &= \text{const} \cdot \exp(-\beta F(A, C)) \\ &= \text{const} \cdot \exp\left[-\frac{1}{2}\beta \frac{\partial^2 F(B^0)}{\partial B_i \partial B_j} (B_i - B_i^0)(B_j - B_j^0)\right], \end{aligned} \quad (5.1.36)$$

with $\beta^{-1} = kT$.

Using (5.1.36) and the notation $\partial^2 F / \partial B_i \partial B_j = u_{ij}$, which is in agreement with (5.1.8a) and (3.1.38), we can find the equilibrium correlator

$$\langle B_i, B_j \rangle = kT u_{ij}^{-1}. \quad (5.1.37)$$

Since $u_{\alpha\sigma} = 0$, we get

$$\langle C, C^\text{T} \rangle = kT \hat{U}_2^{-1} \quad (\hat{U}_2 = \|u_{\rho\sigma}\|). \quad (5.1.38)$$

Comparison of (5.1.35) with (5.1.38) yields

$$-\int_{-\infty}^t \exp[-\hat{D}_2(t-t')] (\hat{L}_2 + \hat{L}_2^\text{T}) \exp[-\hat{D}_2^\text{T}(t-t')] dt' = \hat{U}_2^{-1}. \quad (5.1.39)$$

Let us now find the correlator $\langle \tilde{\eta}(t_1), \tilde{\eta}^\text{T}(t_2) \rangle$ for $t_1 > t_2$. By virtue of (5.1.34, 32c) we obtain

$$\begin{aligned} \langle \tilde{\eta}(t_1) \tilde{\eta}^\text{T}(t_2) \rangle &= -kT \int_{-\infty}^{t_2} \exp[-\hat{D}_2(t_1 - t')] \\ &\quad \times (\hat{L}_2 + \hat{L}_2^\text{T}) \exp[-\hat{D}_2^\text{T}(t_2 - t')] dt', \end{aligned} \quad (5.1.40)$$

or

$$\langle \tilde{\eta}(t_1) \tilde{\eta}^\text{T}(t_2) \rangle = kT \exp[-\hat{D}_2(t_1 - t_2)] \hat{U}_2^{-1} \quad (5.1.41)$$

if we use (5.1.39). We obtain in an analogous manner for $t_1 \leq t_2$:

$$\langle \tilde{\eta}(t_1) \tilde{\eta}^\text{T}(t_2) \rangle = kT \hat{U}_2^{-1} \exp[-\hat{D}_2^\text{T}(t_2 - t_1)]. \quad (5.1.42)$$

Equations (5.1.41, 42) can be combined into one equation

$$\begin{aligned} \langle \tilde{\eta}(t_1) \tilde{\eta}^\text{T}(t_2) \rangle &= kT \exp[-\hat{D}_2(t_1 - t_2)] \hat{U}_2^{-1} \delta(t_1 - t_2) \\ &\quad + kT \hat{U}_2^{-1} \exp[-\hat{D}_2^\text{T}(t_2 - t_1)] \delta(t_2 - t_1), \end{aligned} \quad (5.1.43)$$

where

$$\vartheta(t) = \frac{1}{2}(1 + \text{sign } t) \quad (5.1.44)$$

is the unit step function.

Substituting (5.1.33) into (5.1.30a) and taking into account (5.1.14), we arrive at the Langevin equation

$$\dot{A}_\alpha(t) = - \int \Phi_{\alpha,\beta}(t-t') u_{\beta\gamma} A_\gamma(t') dt' + \zeta_\alpha(t). \quad (5.1.45)$$

where

$$\zeta_\alpha(t) = \xi_\alpha(t) - \hat{D}_{12} \tilde{\eta}(t). \quad (5.1.46)$$

We now find the correlator

$$\begin{aligned} \langle \zeta(t_1) \zeta^T(t_2) \rangle &= \langle \xi(t_1) \xi^T(t_2) \rangle - \hat{D}_{12} \langle \tilde{\eta}(t_1) \xi^T(t_2) \rangle \\ &\quad - \langle \xi(t_1) \tilde{\eta}^T(t_2) \rangle \hat{D}_{12}^T + \hat{D}_{12} \langle \tilde{\eta}(t_1) \tilde{\eta}^T(t_2) \rangle \hat{D}_{12}^T. \end{aligned} \quad (5.1.47)$$

of the random forces (5.1.46). Using (5.1.34, 32b), we easily obtain

$$\langle \tilde{\eta}(t_1) \xi^T(t_2) \rangle = \begin{cases} -kT \exp[-\hat{D}_2(t_1 - t_2)] (\hat{L}_{21} + \hat{L}_{12}^T) & \text{for } t_1 > t_2, \\ 0 & \text{for } t_1 < t_2. \end{cases} \quad (5.1.48)$$

Analogously, we get

$$\langle \xi(t_1) \tilde{\eta}^T(t_2) \rangle = -kT(\hat{L}_{12} + \hat{L}_{21}^T) \exp[-\hat{D}_2^T(t_2 - t_1)] \vartheta(t_2 - t_1). \quad (5.1.49)$$

Using (5.1.32a, 43, 48, 49), we can write down the correlator (5.1.47) in the form

$$\begin{aligned} \beta \langle \zeta(t_1) \zeta^T(t_2) \rangle &= -(\hat{L}_1 + \hat{L}_1^T) \delta(t_{12}) + \hat{D}_{12} \exp(-\hat{D}_2 t_{12}) (\hat{L}_{21} + \hat{L}_{12}^T) \vartheta(t_{12}) \\ &\quad + (\hat{L}_{12} + \hat{L}_{21}^T) \exp(-\hat{D}_2^T t_{21}) \hat{D}_{12}^T \vartheta(t_{21}) \\ &\quad + \hat{D}_{12} \exp(-\hat{D}_2 t_{12}) \hat{U}_2^{-1} \hat{D}_{12}^T \vartheta(t_{12}) \\ &\quad + \hat{D}_{12} \hat{U}_2^{-1} \exp(-\hat{D}_2^T t_{21}) \hat{D}_{12}^T \vartheta(t_{21}). \end{aligned} \quad (5.1.50)$$

Since $\hat{D}_{12} \hat{U}_2^{-1} = -\hat{L}_{12}$ [see (5.1.10)], a number of terms on the right-hand side cancel out and we obtain

$$\begin{aligned} \beta \langle \zeta(t_1) \zeta^T(t_2) \rangle &= -(\hat{L}_1 + \hat{L}_1^T) \delta(t_{12}) + \hat{D}_{12} \exp(-\hat{D}_2 t_{12}) \hat{L}_{21} \vartheta(t_{12}) \\ &\quad + \hat{L}_{21}^T \exp(-\hat{D}_2^T t_{21}) \hat{D}_{12}^T \vartheta(t_{21}). \end{aligned} \quad (5.1.51)$$

Taking into account (5.1.14), we derive

$$\langle \zeta_\alpha(t_1) \zeta_\beta(t_2) \rangle = kT \Phi_{\alpha,\beta}(t_1 - t_2) + kT \Phi_{\beta,\alpha}(t_2 - t_1) \quad (5.1.52)$$

or in shorter form

$$\Phi_{12} = kT(\Phi_{1,2} + \Phi_{2,1}), \quad (5.1.53)$$

where we have used the notation

$$\Phi_{\alpha_1 \alpha_2}(t_1, t_2) = \langle \zeta_{\alpha_1}(t_1) \zeta_{\alpha_2}(t_2) \rangle. \quad (5.1.54)$$

Thus, we find that in the case of relaxation equation (5.1.13) the random forces add up in a standard fashion when we pass to the Langevin equation (5.1.45). The statistical characteristics of these forces are given by (5.1.53), which determines the correlator in terms of the dissipation characteristics $\Phi_{1,2}$. Thus, (5.1.53) is one of the FDRs, namely, a non-Markov linear FDR. We note that if we set $t_1 > t_2$, the formula

$$\langle \zeta_\alpha(t_1) \zeta_\beta(t_2) \rangle = kT \Phi_{\alpha,\beta}(t_1 - t_2), \quad (5.1.55)$$

is valid. The result of this type was first obtained by Mori [5.1].

In the above we have assumed that $A_1(t), \dots, A_r(t)$ are a subset of the components of a “large” Markov process. This assumption is not restrictive. In fact, any non-Markov process can be approximated by a subset of variables of the complex Markov process. The accuracy of the approximation can be improved to any degree of precision by increasing the number of additional components $C(t)$. The form of (5.1.24, 53) is independent of the number of additional components. Consequently, in the limit they will be valid for any arbitrary non-Markov process.

5.1.4 Particular Case of Equations in the Linear–Quadratic Approximation

In the linear–quadratic approximation, one should retain in (5.1.3) linear and quadratic terms in x_α . If, as before, A_α is a part of the components of the combined Markov process $B = (A, C)$, then the latter is described by

$$\dot{B}_i = l_{i,j} x_j + \frac{1}{2} l_{i,jk} x_j x_k. \quad (5.1.56)$$

We suppose that among the coefficients $l_{i,jk}$ only the coefficients $l_{\alpha,\sigma\tau}$ are nonzero and that the values s_{ijk} are equal to zero in the formulas

$$x_i = u_{ij} B_j + \frac{1}{2} s_{ijk} B_j B_k \quad (5.1.57)$$

of the linear–quadratic approximation, so that one can use the simple linear relations (5.1.8). The more general case can be tackled by the same method (in principle), but the calculations are lengthier in the general case. In the particular case considered above, we have from (5.1.56)

$$\dot{A}_\alpha = l_{\alpha,\beta} x_\beta + l_{\alpha,\sigma} u_{\sigma\tau} C_\tau + \frac{1}{2} l_{\alpha,\sigma\tau} u_{\sigma\rho} u_{\tau\pi} C_\rho C_\pi, \quad (5.1.58a)$$

$$\dot{C}_\rho = l_{\rho,\beta} x_\beta + l_{\rho,\sigma} u_{\sigma\tau} C_\tau. \quad (5.1.58b)$$

Here (5.1.58b) coincides with (5.1.9b). For this reason its solution is (5.1.11). Substitution of (5.1.11) into (5.1.58a) gives

$$\begin{aligned} \dot{A}_\alpha(t_1) = & - \int \Phi_{\alpha,\beta}(t_1, t_2) x_\beta(t_2) dt_2 \\ & - \frac{1}{2} \int \Phi_{\alpha,\beta\gamma}(t_1, t_2, t_3) x_\beta(t_2) x_\gamma(t_3) dt_2 dt_3, \end{aligned} \quad (5.1.59)$$

where $\Phi_{\alpha,\beta}$ is defined in (5.1.14), and

$$\Phi_{\alpha,\beta\gamma}(t_1, t_2, t_3) = - l_{\alpha,\sigma\tau} V_{\sigma\rho}(t_{12}) V_{\tau\pi}(t_{13}) l_{\rho,\beta} l_{\pi,\gamma}. \quad (5.1.60)$$

Here we have used the definition

$$\| V_{\sigma\rho}(t) \| = \exp(-\hat{D}_2 t) \vartheta(t). \quad (5.1.61)$$

Here and subsequently $u_{\alpha\beta}$, $u_{\rho\sigma}$ are assumed to be equal to the identity matrix for the sake of compactness of the formulas.

Equation (5.1.59) has the general form corresponding to the linear-quadratic approximation, the functions $\Phi_{1,2}$, $\Phi_{1,23}$ being specified.

We now proceed to equations of the Langevin type. Using a stochastic representation of the Markov processes (see Appendix 7), we consider the set of equations in the linear-quadratic approximation

$$\dot{B}_i = l_{i,j}x_i + \frac{1}{2}l_{i,jk}x_jx_k + \sum_s (\sigma_i^{(s)} + \sigma_{ij}^{(s)}x_j)\xi^{(s)}(t), \quad (5.1.62)$$

which corresponds to (5.1.56). According to (A7.4, 5) the functions

$$\sigma_i^{(s)}(x) = \sigma_i^{(s)} + \sigma_{ij}^{(s)}x_j \quad (5.1.63)$$

are related to $\kappa_{ij}(x) \approx K_{ij}(B(x))$, $\kappa_{ijk} \approx K_{ijk}$ by

$$\kappa_{ij}(x) = \sum_s \sigma_i^{(s)}(x)\sigma_j^{(s)}(x) = \sum_s (\sigma_i^{(s)} + \sigma_{ik}^{(s)}x_k)(\sigma_j^{(s)} + \sigma_{jl}^{(s)}x_l),$$

$$\kappa_{ijk}(x) = \sum_s \sigma_i^{(s)}\sigma_j^{(s)}\sigma_k^{(s)}. \quad (5.1.64)$$

It is supposed that the independent random functions $\xi^{(s)}$ have zero means and the correlators given by

$$\begin{aligned} \langle \xi^{(s)}(t_1)\xi^{(r)}(t_2) \rangle &= \delta_{sr}\delta(t_{12}), \\ \langle \xi^{(s)}(t_1)\xi^{(r)}(t_2)\xi^{(l)}(t_3) \rangle &= \delta_{sr}\delta_{rl}\delta(t_{12})\delta(t_{13}). \end{aligned} \quad (5.1.65)$$

The other correlators are not considered.

Since in the linear-quadratic approximation we can set

$$\kappa_{ij}(x) = l_{ij} + l_{ij,k}x_k, \quad \kappa_{ijk} = l_{ijk}, \quad (5.1.66)$$

we obtain from (5.1.64)

$$\begin{aligned} \sum_s \sigma_i^{(s)}\sigma_j^{(s)} &= l_{ij}, \\ \sum_s (\sigma_{ik}^{(s)}\sigma_j^{(s)} + \sigma_i^{(s)}\sigma_{jk}^{(s)}) &= l_{ij,k}, \\ \sum_s \sigma_i^{(s)}\sigma_j^{(s)}\sigma_k^{(s)} &= l_{ijk}. \end{aligned} \quad (5.1.67)$$

According to (4.1.16, 18) $l_{ij,k}$ and l_{ijk} are expressed in terms of $l_{i,jk}$. When among $l_{i,jk}$ only $l_{\alpha,\sigma\tau}$ are not equal to zero, as in the case (5.1.58), we have

$$\begin{aligned} l_{\alpha\sigma,\tau} &= -kTl_{\alpha,\sigma\tau}, \\ l_{\sigma\tau,\alpha} &= kT\varepsilon_\alpha\varepsilon_\sigma\varepsilon_\tau l_{\alpha,\sigma\tau}, \\ l_{\alpha\sigma\tau} &= 2(kT)^2 \vartheta_{\alpha\sigma\tau}^- l_{\alpha,\sigma\tau}. \end{aligned} \quad (5.1.68)$$

The other coefficients $l_{ij,k}$ and l_{ijk} are equal to zero. The coefficient $l_{\alpha\gamma,\beta} = 0$ i.e. by virtue of (5.1.67)

$$\sum_s (\sigma_{\alpha,\beta}^{(s)} \sigma_\gamma^{(s)} + \sigma_\alpha^{(s)} \sigma_{\gamma,\beta}^{(s)}) = 0 , \quad (5.1.69)$$

which is in agreement with

$$\sigma_{\alpha,\beta}^{(s)} = 0 . \quad (5.1.70)$$

Thus, (5.1.70) is the consequence of the absence of the nonlinear terms $l_{\alpha,\beta\gamma} x_\beta x_\gamma$ in (5.1.58). If, on the contrary, only these nonlinear terms were present in (5.1.58), we would have $\sigma_{\tau,j} = 0$.

Using (5.1.58, 70), we write (5.1.62) as

$$\dot{A}_\alpha = l_{\alpha,\beta} x_\beta + l_{\alpha,\sigma} C_\sigma + \frac{1}{2} l_{\alpha,\sigma\tau} C_\sigma C_\tau + \sum_s (\sigma_\alpha^{(s)} + \sigma_{\alpha,\tau}^{(s)} C_\tau) \xi^{(s)} , \quad (5.1.71a)$$

$$\dot{C}_\rho = l_{\rho,\beta} x_\beta + l_{\rho,\sigma} C_\sigma + \sum_s (\sigma_\rho^{(s)} + \sigma_{\rho,\beta}^{(s)} x_\beta + \sigma_{\rho,\tau}^{(s)} C_\tau) \xi^{(s)} . \quad (5.1.71b)$$

Owing to the smallness of the fluctuations, in the main approximation in k [i.e. with the error $\mathcal{O}(k^2)$] it is not necessary to distinguish whether the stochastic expressions in (5.1.71) are taken in the Ito sense or in the S-sense (see Appendix 7). In other words, we can use (5.1.64, 65) and at the same time treat the random functions $\xi^{(s)}$ in (5.1.71) as ordinary smooth functions in the conventional sense.

Solving (5.1.71b) by iterations to the necessary accuracy, we can find C as a functional of $x_\beta(t)$ and $\xi^{(s)}(t)$. Substitution of this functional into (5.1.71a) yields

$$\dot{A}_\alpha = - \int \Phi_{\alpha,\beta} x_\beta dt_2 - \frac{1}{2} \int \Phi_{\alpha,\beta\gamma} x_\beta x_\gamma dt_2 dt_3 - F_\alpha[t, x, \xi] , \quad (5.1.72)$$

where $F_\alpha[t, x, \xi]$ are functionals of $x_\beta(t)$ and $\xi^{(s)}(t)$; the F_α have zero mean values. Further, one can evaluate the correlators

$$\begin{aligned} \langle F_\alpha[t_1, x, \xi], F_\beta[t_2, x, \xi] \rangle_x &\equiv \Psi_{\alpha\beta}[t_1, t_2, x] \\ &= \Phi_{\alpha\beta}(t_1, t_2) + \int \Phi_{\alpha\beta,\gamma}(t_1, t_2, t_3) x_\gamma(t_3) dt_3 + \dots , \end{aligned} \quad (5.1.73a)$$

$$\langle F_\alpha[t_1, 0, \xi], F_\beta[t_2, 0, \xi] F_\gamma[t_3, 0, \xi] \rangle = \Phi_{\alpha\beta\gamma}(t_1, t_2, t_3) . \quad (5.1.73b)$$

Correlator (5.1.73a) corresponds to the fixed plot of the function $x(t)$. For calculating $\Phi_{\alpha\beta,\gamma}$, one should consider in $\Psi_{\alpha\beta}$ only terms of the first order in kT and linear in x . For calculating $\Phi_{\alpha\beta\gamma}$ one should take into account only the terms that are of the order of $(kT)^2$ and independent of x . This defines the accuracy within which (5.1.71b) need be solved.

5.1.5 Quadratic FDRs

The functions $\Phi_{1,23}$, $\Phi_{12,3}$ and Φ_{123} are connected by two different relations of the quadratic theory. One of these relations has the form

$$\beta\Phi_{12,3} = \Phi_{1,23} + \Phi_{2,13} - \Phi_{3,12}^{\text{t.c.}}, \quad (5.1.74)$$

where the superscript “t.c.”, as in (5.1.23, 25), denotes time conjugation:

$$\Phi_{\alpha_3,\alpha_1\alpha_2}(t_1, t_2, t_3)^{\text{t.c.}} = \varepsilon_{\alpha_1}\varepsilon_{\alpha_2}\varepsilon_{\alpha_3} \Phi_{\alpha_3,\alpha_1\alpha_2}(-t_1, -t_2, -t_3). \quad (5.1.75)$$

Let us check the validity of (5.1.74) in the case of (5.1.71). In (5.1.72) one need consider only the terms linear in ξ . Equation (5.1.71b) can be taken as

$$\dot{C}_\rho = l_{\rho,\beta}x_\beta + l_{\rho,\sigma}C_\sigma + \sum_s (\sigma_\rho^{(s)} + \sigma_{\rho,\beta}^{(s)}x_\beta + \sigma_{\rho,\tau}^{(s)}C_\tau^0)\xi^{(s)}, \quad (5.1.76)$$

where [see (5.1.11)]

$$C_\tau^0(t_1) = \int_{-\infty}^{t_1} V_{\tau\pi}(t_{12})l_{\pi,\beta}x_\beta(t_2)dt_2. \quad (5.1.77)$$

Substituting the solution

$$\begin{aligned} C_\rho(t_1) &= C_\rho^0(t_1) + \int_{-\infty}^{t_1} V_{\rho\pi}(t_{12}) \sum_s [\sigma_\pi^{(s)} + \sigma_{\pi,\beta}^{(s)}x_\beta(t_2) \\ &\quad + \sigma_{\pi,\tau}^{(s)}C_\tau^0(t_2)]\xi^{(s)}(t_2)dt_2 \end{aligned} \quad (5.1.78)$$

of (5.1.76) into (5.1.71a), we obtain (5.1.72) as

$$\begin{aligned} -F_{\alpha_1}[t_1, x, \xi] &= \sum_s \{ [\sigma_{\alpha_1}^{(s)} + \sigma_{\alpha_1,\beta}^{(s)}x_\beta + \sigma_{\alpha_1,\tau}^{(s)}V_{\tau\pi}l_{\pi,\gamma}x_\gamma]\xi^{(s)} \\ &\quad + l_{\alpha_1,\sigma}V_{\sigma\pi}[\sigma_\pi^{(s)} + \sigma_{\pi,\beta}^{(s)}x_\beta + \sigma_{\pi,\tau}^{(s)}V_{\tau\phi}l_{\phi,\gamma}x_\gamma]\xi^{(s)} \\ &\quad + l_{\alpha_1,\rho\tau}V_{\rho\pi}l_{\pi,\beta}x_\beta V_{\tau\phi}\sigma_\phi^{(s)}\xi^{(s)} \} . \end{aligned} \quad (5.1.79)$$

Here the integrals over time are implied (the integrals will not be necessary if we proceed to the spectral representation). One can write another expression analogous to (5.1.79), but with the subscript 1 replaced by the subscript 2. Both expressions can be substituted into the correlator $\langle F_{\alpha_1}, F_{\alpha_2} \rangle$. In order to calculate the part $\Phi_{12,3}x_3$ of the last correlator one should take the terms linear in x . We obtain

$$\langle F_{\alpha_1}, F_{\alpha_2} \rangle = T_1 + T_2 + T_3 + T_4 + \dots, \quad (5.1.80)$$

where

$$\begin{aligned} T_1 &= l_{\alpha_1,\sigma}V_{\sigma\pi}l_{\alpha_2,\rho}V_{\rho\phi}\sum_s(\sigma_\pi^{(s)}\sigma_{\phi,\beta}^{(s)} + \sigma_{\pi,\beta}^{(s)}\sigma_\phi^{(s)})x_\beta, \\ T_2 &= l_{\alpha_1,\rho\tau}V_{\tau\phi}\sum_s(\sigma_\phi^{(s)}\sigma_{\alpha_2}^{(s)})V_{\rho\pi}l_{\pi,\beta}x_\beta + \text{tran. (1, 2)}, \\ T_3 &= l_{\alpha_1,\sigma}V_{\sigma\pi}\sum_s(\sigma_{\pi,\tau}^{(s)}\sigma_{\alpha_2}^{(s)} + \sigma_\pi^{(s)}\sigma_{\alpha_2,\tau}^{(s)})V_{\tau\rho}l_{\rho,\beta}x_\beta + \text{tran. (1, 2)}, \\ T_4 &= l_{\alpha_1,\sigma}V_{\sigma\pi}l_{\alpha_2,\rho\tau}V_{\tau\phi}\sum_s(\sigma_\pi^{(s)}\sigma_\phi^{(s)})V_{\rho\psi}l_{\psi,\beta}x_\beta + \text{tran. (1, 2)}. \end{aligned} \quad (5.1.81)$$

Here “tran. (1, 2)” means the addition of analogous terms with an interchange of subscripts 1 and 2. In (5.1.80), the terms not explicitly written out are of no

importance to us, say, the terms independent of x . A number of pairings vanishes; for example, the pairing of the term containing $\sigma_{\alpha_1}^{(s)}$ with the term containing $\sigma_{\tau,\beta}^{(s)}$ vanishes since $l_{\alpha,\beta} = 0$. The products of the type $\sigma\sigma$ are transformed by means of (5.1.67) and equations

$$\sum_s \sigma_i^{(s)} \sigma_j^{(s)} = l_{ij} = kT(l_{i,j} + l_{j,i}).$$

The expression for T_1 assumes the form

$$\beta T_1 = l_{\alpha_1,\sigma} V_{\rho\pi} l_{\alpha_2,\rho} V_{\rho\varphi} \varepsilon_\pi \varepsilon_\varphi \varepsilon_\beta l_{\beta,\pi\varphi} x_\beta. \quad (5.1.82)$$

Hence, as a consequence of the formulas $V_{\sigma\pi} \varepsilon_\pi = \varepsilon_\sigma V_{\pi\sigma}$, $l_{\alpha,\sigma} \varepsilon_\sigma = l_{\sigma,\alpha} \varepsilon_\alpha$ [see (5.1.18, 19)] one obtains

$$\begin{aligned} \beta T_1 &= \varepsilon_{\alpha_1} \varepsilon_{\alpha_2} \varepsilon_\beta \int V_{\pi\sigma}(t_{13}) l_{\sigma,\alpha_1} V_{\varphi\rho}(t_{23}) l_{\rho,\alpha_2} l_{\beta,\pi\varphi} x_\beta(t_3) dt_3 \\ &= \varepsilon_{\alpha_1} \varepsilon_{\alpha_2} \varepsilon_\beta \int x_\beta(t_3) l_{\beta,\pi\varphi} V_{\pi\sigma}(-t_{31}) V_{\varphi\rho}(-t_{23}) l_{\sigma,\alpha_1} l_{\rho,\alpha_2} dt_3 \\ &= -x_3 \Phi_{3,12}^{\text{t.c.}}. \end{aligned} \quad (5.1.83)$$

Here (5.1.60) and the definition of the time conjugation (5.1.75) have been used. Furthermore, it is easy to see that the expression

$$-l_{\alpha_1,\rho\tau} V_{\tau\varphi}(l_{\varphi,\alpha_2} + l_{\alpha_2,\varphi}) V_{\rho\pi} l_{\pi,\beta} x_\beta \quad (5.1.84)$$

appearing in T_2 contains the function $\Phi_{\alpha_1,\alpha_3\beta} x_\beta$. Therefore, (5.1.80) can be written as

$$\beta \langle F_{\alpha_1}, F_{\alpha_2} \rangle_x = (\Phi_{\alpha_1,\alpha_2\beta} + \Phi_{\alpha_2,\alpha_1\beta} - \Phi_{\beta,\alpha_1\alpha_2}^{\text{t.c.}}) x_\beta + R, \quad (5.1.85)$$

where R denotes the sum of the remainder terms:

$$\begin{aligned} R &= -l_{\alpha_1,\sigma} K_{\sigma\varphi} l_{\alpha_2,\varphi\tau} V_{\tau\rho} l_{\rho,\beta} x_\beta + \text{tran. (1, 2)}, \\ \|K_{\sigma\varphi}(i\omega)\| &= \hat{V}^T(-i\omega) + \hat{V}(i\omega) + \hat{V}(i\omega) \|l_{\sigma,\varphi} + l_{\varphi,\sigma}\| \hat{V}^T(-i\omega). \end{aligned} \quad (5.1.86)$$

Here the superscript T denotes transposition:

$$\|V_{\sigma\varphi}\|^T = \|V_{\varphi\sigma}\|; \quad (5.1.87)$$

$\hat{K}(i\omega)$ and $\hat{V}(i\omega)$ are defined by

$$\begin{aligned} \hat{K}(i\omega) &= \int \exp(-i\omega t_{12}) \hat{K}(t_{12}) dt_{12}, \\ \hat{V}(i\omega) &= \int \exp(-i\omega t_{12}) \hat{V}(t_{12}) dt_{12}. \end{aligned} \quad (5.1.88)$$

On the right-hand side of (5.1.86) the terms resulting from T_2 , T_3 , T_4 are written successively. Expression (5.1.86) can be transformed to

$$\hat{K}(i\omega) = \hat{V}(i\omega) \{[\hat{V}(i\omega)]^{-1} + [\hat{V}^T(-i\omega)]^{-1} + \hat{L}_2 + \hat{L}_2^T\} \hat{V}^T(-i\omega). \quad (5.1.89)$$

It is easy to verify that the expression in the braces is equal to zero for the matrix $\hat{V}(i\omega) = (i\omega\hat{I} - \hat{L}_2)^{-1}$ corresponding to (5.1.61) for $\hat{U}_2 = \hat{I}$ where \hat{I} is the identity matrix. Thus, the remainder terms vanish, so that we obtain (5.1.74) from (5.1.85, 73a). Besides (5.1.74), the three-subscript functions Φ_{\dots} satisfy the relation

$$\beta^2 \Phi_{123} = \Phi_{1,23} - \Phi_{1,23}^{t,c} + \Phi_{2,34} - \Phi_{2,34}^{t,c} + \Phi_{3,12} - \Phi_{3,12}^{t,c}. \quad (5.1.90)$$

Its proof is lengthier than in the case of (5.1.71), and we will not consider it.

5.1.6 General Definition of the Functions Φ_{\dots}

Let the stochastic equation

$$\dot{B}_\alpha(t) = -F_\alpha[t, \Xi, x(B)],$$

i.e.

$$\dot{B}_1 = -F_1[\Xi, x(B)], \quad (5.1.91)$$

correspond to (5.1.2) written for the means $A_\alpha = \langle B_\alpha \rangle$. Here $\Xi(t)$ is a set of random functions. By virtue of (5.1.91) the correlations between $B(t)$ and $\Xi(t)$ are formed. Let us now consider the expression $F_1[\Xi, x]$ before its substitution into (5.1.91). As yet, $B(t)$ and $\Xi(t)$ are not correlated, and the function $x(t)$ can be regarded as an independent argument of the functional. This function can be fixed without distorting the statistical properties of the noises Ξ . After fixing $x(\cdot)$ we can find the correlators

$$\langle F_1[\Xi, x], \dots, F_m[\Xi, x] \rangle_x = \Psi_{1\dots m}[x], \quad m = 1, 2, \dots \quad (5.1.92)$$

which are functionals of $x(t)$. The functions $\Phi_{1\dots m, (m+1)\dots(m+n)}$ are defined as the coefficients of the functional Taylor series expansion

$$\Psi_{1\dots m}[x(t)] = \sum_{n=0}^{\infty} \frac{1}{n!} \Phi_{1\dots m, (m+1)\dots(m+n)} x_{m+1} \dots x_{m+n}. \quad (5.1.93)$$

The functions $\Phi_{1,2}$, Φ_{12} , $\Phi_{1,23}$, $\Phi_{12,3}$ and Φ_{123} considered previously are in agreement with this definition.

A variety of stochastic representations (5.1.91) and various expressions $F_1[\Xi, x]$ are possible for a given random process $\{B_\alpha(t)\}$. However, we must have identical functions Φ_{\dots} for these various equivalent stochastic representations. The simplest stochastic representation can be written as

$$\dot{B}_1 = -\Psi_1[x] - \sum_s \int S_{1t}^{(s)}[x] \xi^{(s)}(t) dt. \quad (5.1.94)$$

By analogy with (A7.5) we have

$$\Psi_{1\dots m}[x] = \sum_s \int S_{1t}^{(s)}[x] \dots S_{mt}^{(s)}[x] dt, \quad m \geq 2. \quad (5.1.95)$$

Random functions $\xi^{(s)}(t)$ are assumed to be statistically independent and to have zero means, and their correlators are given by

$$\langle \xi^{(s_1)}(t_1), \dots, \xi^{(s_m)}(t_m) \rangle = \delta_{s_1 \dots s_m} \delta(t_1, \dots, t_m), \quad (5.1.96)$$

where

$$\delta_{s_1 \dots s_m} = \delta_{s_1 s_2} \dots \delta_{s_1 s_m}, \quad \delta(t_1, \dots, t_m) = \delta(t_{12}) \dots \delta(t_{1m}). \quad (5.1.97)$$

The universal relations connecting the functions Φ_{\dots} will be called the FDRs of the first kind. Formulas (5.1.25, 53, 74, 90) are examples of such relations. These relations are generalizations of the Markov theory relations (4.1.12, 13, 16, 18) to the non-Markov case. If (5.1.91–93) are applied to the Markov process, the right-hand side of (5.1.94) must depend on $x(t_1)$ without inertia, i.e. the functionals $S_1^{(s)}[x]$ must be of the form

$$S_{1t}^{(s)}[x] \equiv S_{\alpha_1 t_1 t}^{(s)}[x] = -\sigma_{\alpha_1}^{(s)}(x(t_1))\delta(t_1 - t). \quad (5.1.98)$$

In this case the stochastic expression (5.1.94) can be understood, say, in the sense of equation (A7.3). From (5.1.95, 98) we obtain

$$\Psi_{\alpha_1 t_1 \dots \alpha_m t_m}[x] = (-1)^m \kappa_{\alpha_1 \dots \alpha_m}(x(t_1))\delta(t_1, \dots, t_m), \quad (5.1.99a)$$

$$\begin{aligned} \Phi_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n}(t_1, \dots, t_{m+n}) \\ = (-1)^m l_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} \delta(t_1, \dots, t_{m+n}). \end{aligned} \quad (5.1.99b)$$

Relations (5.1.25, 53, 74, 90) go over into (4.1.13, 12, 16, 18), respectively. Therefore, we can say that the relations obtained in Sect. 4.1.2 are the FDRs of the first kind in the case of Markov processes.

From the principle of correspondence between the relations of the non-Markov theory and those of the Markov theory, it can be concluded that the following four-subscript formulas, which are analogous to (4.1.27–29, 31), must hold:

$$\begin{aligned} \beta \Phi_{12,34} &= \Phi_{1,234} + \Phi_{2,134} + C_{12,34}, \quad C_{12,34} = C_{34,12}^{\text{t.c.}}, \\ \beta^2 \Phi_{123,4} &= \Phi_{1,234} + \Phi_{2,134} + \Phi_{3,124} + \Phi_{4,123}^{\text{t.c.}} + C_{12,34} + C_{13,24} + C_{23,14}, \\ \beta^3 \Phi_{1234} &= P_{(1234)} \Phi_{12,34} + C_{12,34} + C_{13,24} + C_{23,14} + \text{t.c.}, \end{aligned} \quad (5.1.100)$$

where $P_{(1234)}$ denotes a sum (containing four terms) over cyclic permutations of subscripts 1, 2, 3, 4 and “+ t.c.” means the addition of the time-conjugate terms.

In (5.1.100), $C_{12,34}$ is the dissipationally undeterminable function, i.e. the function that cannot be found when only $\Phi_{1,234}$ is known. It is determined by $\Phi_{12,34}$ and $\Phi_{1,234}$. Eliminating $C_{12,34}$ from (5.1.100), we obtain three equations.

We shall return to the FDRs of the first kind in Sect. 5.5. There the connection between the FDRs of the first and second kinds will be established.

5.1.7 Generating Functional and Generating Equation

We now define the generating functional $\Pi[y(\cdot), x(\cdot)]$ whose arguments are the functions $x_1 = x_{\alpha_1}(t_1)$ and $y_1 = y_{\alpha_1}(t_1)$ in the following way:

$$\begin{aligned} \Pi[y, x] &= \sum_{\substack{m \geq 1 \\ n \geq 0}} \frac{1}{m! n!} (kT)^{-m+1} \Phi_{1 \dots m, (m+1) \dots (m+n)} \\ &\quad \times y_1 \dots y_m x_{m+1} \dots x_{m+n}. \end{aligned} \quad (5.1.101)$$

If we consider (5.1.93), we get

$$\Pi[y, x] = \sum_{m=1}^{\infty} \frac{1}{m!} (kT)^{-m+1} \Psi_{1\dots m}[x] y_1 \dots y_m . \quad (5.1.102)$$

From (5.1.101) it is seen that the functions Φ_{\dots} can be obtained by functional differentiation of the generating functional at the “zero point”. Using (5.1.99), (3.1.41) and (4.1.6), we easily find that in the Markov case the generating functional is related to the kinetic potential image by

$$\Pi[y, x] = \int R[-y(t), x(t)] dt . \quad (5.1.103)$$

It is natural to expect that owing to the applicability of the equilibrium probability densities and time reversibility, the functional (5.1.101) satisfies a generating equation, which is a generalization of (3.2.50) to the non-Markov case. Using the principle of the analogy between the non-Markov theory and the Markov one and considering (5.1.103), we easily conclude that the non-Markov generating equation must have the form

$$\Pi[y - x, x] = \Pi[-y^{t.c.}, x^{t.c.}] , \quad (5.1.104)$$

where, as before, “t.c.” means the operation of time conjugation, i.e.

$$x_{\alpha_1}(t_1)^{t.c.} = \varepsilon_{\alpha_1} x_{\alpha_1}(-t_1) . \quad (5.1.105)$$

From (5.1.104) all FDRs of the first kind can be obtained. In doing so, we note that

$$\begin{aligned} \Phi_{1\dots(m+n)} y_1^{t.c.} \dots y_m^{t.c.} x_{m+1}^{t.c.} \dots x_{m+n}^{t.c.} \\ = \Phi_{1\dots(m+n)}^{t.c.} y_1 \dots y_m x_{m+1} \dots x_{m+n} . \end{aligned} \quad (5.1.106)$$

When time symmetry is absent, instead of (5.1.104) we must employ the weaker equality [cf. (3.1.36)].

$$\Pi[-x, x] = 0 . \quad (5.1.107)$$

In this case, the reciprocal relation (5.1.25) is not necessarily valid, but (5.1.53) retains its validity, and instead of three-subscript relations (5.1.74, 90) we have only one relation:

$$\beta^2 \Phi_{123} = \beta \Phi_{12,3} + \beta \Phi_{13,2} + \beta \Phi_{23,1} - \Phi_{1,23} - \Phi_{2,13} - \Phi_{3,12} . \quad (5.1.108)$$

One relation remains valid also in the cubic case.

5.1.8 The *H*-Theorem of Non-Markov Theory

Let the function $A(t)$ be the solution of the equation

$$\dot{A}_{\alpha} = -\Psi_{\alpha}\{x[A(t)]\delta(t-t_0)\} , \quad (5.1.109)$$

which is analogous to (5.1.2), with the initial condition

$$A_{\alpha}(t_0) = A_{\alpha}^{in} . \quad (5.1.110)$$

The truncating function (5.1.44) appears here since the values $A(t)$ are not defined for $t < t_0$. We consider the free-energy increment for $t_1 > t_0$:

$$\Delta F = F(A(t_1)) - F(A(t_0)). \quad (5.1.111)$$

This increment can be written as

$$\Delta F = \int_{t_0}^{t_1} \frac{\partial F}{\partial A} \dot{A} dt = \int_{t_0}^{t_1} x(A(t)) \dot{A}(t) dt. \quad (5.1.112)$$

Here (3.1.38) has been used. Substituting (5.1.109) into the right-hand side of (5.1.112) and setting

$$\tilde{x}(t) = \begin{cases} x(A(t)) & \text{for } t_0 < t < t_1, \\ 0 & \text{for } t < t_0 \text{ or } t > t_1, \end{cases} \quad (5.1.113)$$

we obtain

$$\Delta F = -\Psi_1[\tilde{x}] \tilde{x}_1. \quad (5.1.114)$$

The statement of the H -theorem is as follows: from (5.1.107) it follows that

$$\Delta F \leq 0. \quad (5.1.115)$$

Proof. Let the argument function in (5.1.107) be chosen as in (5.1.113). We then get

$$\Pi[-\tilde{x}, \tilde{x}] = 0. \quad (5.1.116)$$

We let $x(t) = \tilde{x}(t)$ in (5.1.92). Carrying out the summation, according to (5.1.102, 92) we obtain

$$\Pi[y, \tilde{x}] = kT \sum_{m=1}^{\infty} \frac{\beta^m}{m!} \langle y_1 F_1[\Xi, \tilde{x}], \dots, y_m F_m[\Xi, \tilde{x}] \rangle_{\tilde{x}}. \quad (5.1.117)$$

Hence, by virtue of the formulas of the type (2.1.10, 2) we find

$$\Pi[y, \tilde{x}] = kT \ln \langle \exp \{ \beta y_1 F_1[\Xi, \tilde{x}] \} \rangle_{\tilde{x}}. \quad (5.1.118)$$

Setting $y = -\tilde{x}$ and taking into account (5.1.116), we have

$$\ln \langle \exp \{ -\beta \tilde{x}_1 F_1[\Xi, \tilde{x}] \} \rangle_{\tilde{x}} = 0, \quad \langle \exp \{ -\beta \tilde{x}_1 F_1[\Xi, \tilde{x}] \} \rangle_{\tilde{x}} = 1. \quad (5.1.119)$$

This can be written as

$$\langle \beta \tilde{x}_1 F_1[\Xi, \tilde{x}] \rangle_{\tilde{x}} = \langle \exp \{ -\beta \tilde{x}_1 F_1[\Xi, \tilde{x}] \} + \beta \tilde{x}_1 F_1[\Xi, \tilde{x}] - 1 \rangle_{\tilde{x}}. \quad (5.1.120)$$

By virtue of (5.1.92) the mean $\langle F_1(\Xi, \tilde{x}) \rangle_{\tilde{x}}$ coincides with $\Psi_1(\tilde{x})$. Since the function $\exp(-z) - 1 + z$ is nonnegative, the right-hand side of (5.1.120) is nonnegative, so that $\beta \tilde{x}_1 \Psi_1(\tilde{x}) \geq 0$. By virtue of (5.1.114) this inequality gives (5.1.115).

Inequality (5.1.115) corresponds to the energy version of the theory. In the entropy version we would have the inequality $\Delta S \geq 0$. This H -theorem is the generalization of the theorem of Sect. 4.6.3 to the non-Markov case.

5.1.9 Covariant Form of Non-Markov FDRs of the First Kind

The non-Markov FDRs of the first kind, just like the Markov FDRs, can also be applied to the case when the internal parameters $B = \{B_\alpha\}$ are the curvilinear coordinates of a space with a metric tensor $g_{\alpha\beta}(B)$ which is independent of time. Then the FDRs can be written in the tensor-covariant form. We shall regard the parameters B , as we have done in Sects. 4.2.3–5, as contravariant vectors and write them as B^α .

At first we note that formula (5.1.1), which is the starting point for the theory of this section, should now be written as

$$\dot{A}^\alpha(t) = -f^\alpha[t, A(\cdot)]. \quad (5.1.121)$$

The corresponding stochastic equation reads

$$\dot{B}^\alpha(t) = -F^\alpha[t, \Xi(\cdot), B(\cdot)]. \quad (5.1.122)$$

Here f^α and F^α have the transformation properties of a contravariant vector. We assume that the $B^\alpha(t)$ are identically transformed for all t .

By analogy with (5.1.92) we introduce the notations

$$\begin{aligned} & \langle F^{\alpha_1}[t_1, \Xi(\cdot), B(\cdot)], \dots, F^{\alpha_m}[t_m, \Xi(\cdot), B(\cdot)] \rangle_{B(\cdot)} \\ &= f^{\alpha_1 \dots \alpha_m}[t_1, \dots, t_m, B(\cdot)]. \end{aligned} \quad (5.1.123)$$

Here $f^{\alpha_1 \dots \alpha_m}$ are contravariant tensors, and the function $B(t)$ is supposed to be fixed and independently pre-assigned. In the non-Markov theory we consider the functional

$$f^{\alpha_1 \dots \alpha_m}[t_1, \dots, t_m, B(\cdot)] \equiv f^1 \dots ^m[B(\cdot)]$$

instead of the functions $K_{\alpha_1 \dots \alpha_m}(B)$ of the Markov theory. We now need to consider the functional derivatives

$$\delta^n f^{\alpha_1 \dots \alpha_m}[t_1, \dots, t_m, B(\cdot)] / \delta B^{\beta_1}(t'_1) \dots \delta B^{\beta_n}(t'_n) \quad (5.1.124)$$

instead of the partial derivatives $\partial^n K_{\alpha_1 \dots \alpha_m}(B) / \partial B_{\beta_1} \dots \partial B_{\beta_n}$ or (in a more exact form)

$$\partial^n K^{\alpha_1 \dots \alpha_m}(B) / \partial B^{\beta_1} \dots \partial B^{\beta_n}, \quad (5.1.125)$$

which appear in the formulas of Sect. 4.2. The derivatives (5.1.124) have approximately the same transformation properties as those in (5.1.125) (recall that $K^{\alpha_1 \dots \alpha_m}(B)$ are contravariant tensors only in the first approximation). The derivatives (5.1.124), like those in (5.1.125), are not tensors when $f^{\alpha_1 \dots \alpha_m}$ has tensor properties. As is well known, for obtaining tensor properties one should introduce the covariant derivatives

$$\begin{aligned} (a^{\alpha_1 \dots \alpha_n})_\beta &= \frac{\partial a^{\alpha_1 \dots \alpha_n}}{\partial B^\beta} + \Gamma_{\beta\mu}^{\alpha_i} a^{\mu\alpha_2 \dots \alpha_n} \\ &+ \dots + \Gamma_{\beta\mu}^{\alpha_n} a^{\alpha_1 \dots \alpha_{n-1}\mu}. \end{aligned} \quad (5.1.126)$$

In an analogous fashion we introduce covariant functional derivatives

$$(a^{\alpha_1 \dots \alpha_n}[B(\cdot)])_{;\beta}^{(t_0)} = \frac{\delta a^{\alpha_1 \dots \alpha_n}[B]}{\partial B^\beta(t_0)} + \Gamma_{\beta\mu}^{\alpha_1} a^{\mu\alpha_2 \dots \alpha_n}[B] + \dots \\ + \Gamma_{\beta\mu}^{\alpha_n} a^{\alpha_1 \dots \alpha_{n-1}\mu}[B], \quad (5.1.127)$$

which have tensor properties as in (5.1.126).

Using the definition (5.1.127), we easily extend the method of the derivation of the covariant Markov FDRs, which has been given in Sects. 4.2.3–5, to the case of the FDRs of the first kind. By analogy with (4.2.24), the linear relations (5.1.25, 53) can be written as

$$\{f^\alpha[t_1, B(\cdot)]\}_{;\gamma}^{(t_2)} r^{\gamma\beta} = \{(f^\beta[t_2, B(\cdot)])_{;\gamma}^{(t_1)} r^{\gamma\alpha}\}^{\text{t.c.}} \\ f^{\alpha\beta}[t_1, t_2, B(\cdot)] = kT \{ (f^\alpha[t_1, B(\cdot)])_{;\gamma}^{(t_2)} r^{\gamma\beta} + (f^\beta[t_2, B(\cdot)])_{;\gamma}^{(t_1)} r^{\gamma\alpha} \} \\ \text{for } B(t) = B^0, \quad (5.1.128)$$

where $r^{\gamma\beta}$ have the same meaning as in (4.2.25).

It is easy to understand how the cubic FDRs of the first kind can be written in a covariant form. By analogy with (4.2.33) we see that for obtaining covariant quadratic FDRs we should make the substitutions

$$\Phi_{123} \rightarrow f^{\alpha_1 \alpha_2 \alpha_3}[t_1, t_2, t_3, B^0] \quad (5.1.129a)$$

$$\Phi_{12,3} \rightarrow \{f^{\alpha_1 \alpha_2}[t_1, t_2, B(\cdot)]\}_{;\gamma}^{(t_3)} r^{\gamma\alpha_3} \quad \text{for } B(t) = B^0, \quad (5.1.129b)$$

$$\Phi_{1,23} \rightarrow \{ ((f^{\alpha_1}[t_1, B(\cdot)])_{;\rho}^{(t_2)})_{;\sigma}^{(t_3)} \\ - (f^{\alpha_1}[t_1, B(\cdot)])_{;\mu}^{(t_2)} r^{\mu\nu} [(F_\nu)_{;\rho}],_{;\sigma} \delta(t_{23}) \} \\ \times r^{\rho\alpha_2} r^{\sigma\alpha_3} \quad \text{for } B(t) = B^0 \quad (5.1.129c)$$

into (5.1.74, 90).

In conclusion we note that the FDRs of the second and third kinds, which will be considered later, can also be written in a covariant form.

5.2 Definition of Admittance and Auxiliary Formulas

5.2.1 External Forces and Admittances

The forces x_α conjugate to the internal parameters $B_\alpha(z)$ have been regarded as functions of the means $A_\alpha = \langle B_\alpha \rangle$. Transformations from A to x and from x to A constitute simply a change of variables. We now suppose that real external forces $h_\alpha(t)$, which vary in time and are independent quantities, act on the system S. These forces are the conjugates of $B_\alpha(z)$. They are defined by the equation

$$\mathcal{H}(z, h(t)) = \mathcal{H}_0(z) - \sum_{\alpha=1}^r B_\alpha(z) h_\alpha(t) \equiv \mathcal{H}_0(z) + V. \quad (5.2.1)$$

Here $\mathcal{H}_0(z)$ is the time-independent Hamiltonian that describes the evolution of the system in the absence of the external forces [$h(t) \equiv 0$]. Until now we have supposed that the system under study evolves in the absence of forces. We now suppose that the system evolves according to the Hamiltonian (5.2.1), i.e. its evolution is described by the Hamilton equations with the Hamiltonian (5.2.1). In this case the statistical characteristics of the process $\{B_\alpha(t)\}$ depend on $h_\alpha(t)$. In particular, the means $A_\alpha(t) = \langle B_\alpha(t) \rangle$ are functionals of $h_\alpha(t)$. Expansion of this functional in a functional Taylor series yields

$$\begin{aligned} A_{\alpha_1}[t_1, h] &= A_{\alpha_1}^0 + \int G_{\alpha_1, \alpha_2}(t_1; t_2) h_{\alpha_2}(t_2) dt_2 \\ &\quad + \frac{1}{2} \int G_{\alpha_1, \alpha_2, \alpha_3}(t_1; t_2, t_3) h_{\alpha_2}(t_2) h_{\alpha_3}(t_3) dt_2 dt_3 + \dots, \end{aligned} \quad (5.2.2)$$

where

$$G_{\alpha_1, \alpha_2 \dots \alpha_m}(t_1; t_2, \dots, t_m) = \frac{\delta^{m-1} A_{\alpha_1}[t_1, h]}{\delta h_{\alpha_2}(t_2) \dots \delta h_{\alpha_m}(t_m)} \quad \text{at } h(t) \equiv 0. \quad (5.2.3)$$

The functions (5.2.3) will be called admittances.

Denoting, as previously, each pair (α_j, t_j) by one subscript j , we can write (5.2.2) in the shorter form

$$A_1 = G_{1,2} h_2 + \frac{1}{2} G_{1,23} h_2 h_3 + \frac{1}{6} G_{1,234} h_2 h_3 h_4 + \dots \quad (5.2.4)$$

Here A^0 are assumed to be equal to zero. From (5.2.3) we see that the admittances are symmetrical in the subscripts that stand after the comma; i.e.

$$G_{1,23} = G_{1,32}, \quad G_{1,234} = G_{1,342} = G_{1,432}. \quad (5.2.5)$$

The other functions $G_{1 \dots m, (m+1) \dots n}$ introduced later will have analogous symmetry properties. Further, the law of causality requires that

$$G_{1,2 \dots m} = 0 \quad \text{for } t_1 < \max(t_2, \dots, t_m). \quad (5.2.6)$$

Along with the admittances (5.2.3), we can introduce the modified admittances

$$Y_{1,2 \dots m} = \frac{\partial}{\partial t_1} G_{1,2 \dots m} \equiv p_1 G_{1,2 \dots m}. \quad (5.2.7)$$

In certain cases the use of modified admittances is preferable. On differentiating (5.2.4) with respect to time t_1 and using (5.2.7) we get

$$J_1 = Y_{1,2} h_2 + \frac{1}{2} Y_{1,23} h_2 h_3 + \frac{1}{6} Y_{1,234} h_2 h_3 h_4 + \dots \quad (5.2.8)$$

This is the modified form of (5.2.4). The derivatives $J_1 = (\partial/\partial t_1) A_1$, and also the derivatives without averaging, $\tilde{J}_1 = (\partial/\partial t_1) B_1$, will be called fluxes. Modified admittances (5.2.7) satisfy, naturally, the causality conditions analogous to (5.2.6).

5.2.2 Admittances in the Spectral Representation

If the subscripts $1, 2, \dots$ refer to the pairs $(\alpha_1, t_1), (\alpha_2, t_2), \dots$ in (5.2.4), (5.1.4, 74) etc., we say that these formulas are written in the time representation. However,

these subscripts could also stand for the pairs $(\alpha_1, \omega_1), (\alpha_2, \omega_2), \dots$ which corresponds to the spectral representation. The formulas written by using the integer subscripts do not change when the representation is changed. Likewise, the basic formulas of quantum mechanics remain unchanged when the representation is changed. In order to have invariance with respect to a change of representation, transformation to another representation must be made according to the rule described below.

The integral $-\int V dt$ of the subtrahend in (5.2.1) can be abbreviated as $h_1 B_1$. The theory is invariant under nondegenerate linear transformations (not necessarily real)

$$B_1 \rightarrow A_1^2 B_2 . \quad (5.2.9)$$

If the vector B_1 is assumed to be covariant, the vector h_1 must be contravariant in order that the expression $B_1 h_1$ be invariant. It is preferable to write the vector h with a superscript: h^1 . It would also be better to write x_2 in (5.1.4) and elsewhere as x^2 . We however write h_1 and x_2 since the superscript can be confused with a power. Under the transformations (5.2.9), contravariant vectors transform as

$$h^1 \rightarrow h^2 A_2^1 = (A_2^1)^T h^2 , \quad (5.2.10)$$

where $A_2^1 A_1^3 = I_2^3$; I_2^3 is the identity operator. The admittances are covariant tensors in this case. There are contravariant tensors in the theory as well. These are the impedances $Q^{1,2,\dots,m}$ and $Z^{1,2,\dots,m}$, which will be introduced in Sect. 5.6.

The transition to the time spectrum

$$B_1 \equiv B_{\alpha_1}(\omega_1) = (2\pi)^{-1/2} \int \exp(-i\omega_1 t_1) B_{\alpha_1}(t_1) dt_1 \quad (5.2.11)$$

and also the transition to the space–time spectrum

$$B_1 \equiv B_{j_1}(\mathbf{k}_1, \omega_1) = (2\pi)^{-2} \int \exp(-i\omega_1 t_1 + i\mathbf{k}_1 \cdot \mathbf{r}_1) B_{j_1}(\mathbf{r}_1, t_1) d\mathbf{r}_1 dt_1 \quad (5.2.12)$$

are examples of the transformation (5.2.9).

The latter is applicable to the case when the radius vector \mathbf{r} is among α [$\alpha = (j, \mathbf{r})$]. The transformations (5.2.11, 12) are chosen to be unitary. In the case (5.2.11) the transformation (5.2.10) of a contravariant vector is as follows:

$$h^1 \equiv h^{\alpha_1}(\omega_1) = (2\pi)^{-1/2} \int \exp(i\omega_1 t_1) h^{\alpha_1}(t_1) dt_1 . \quad (5.2.13)$$

The admittances, like the covariant tensors, transform in the following way:

$$\begin{aligned} G_{1,2,\dots,m} &\equiv G_{\alpha_1,\alpha_2,\dots,\alpha_m}(\omega_1, \dots, \omega_m) \\ &= (2\pi)^{-m/2} \int \exp(-i\omega_1 t_1 - \dots - i\omega_m t_m) G_{\alpha_1,\alpha_2,\dots,\alpha_m} \\ &\quad \times (t_1, \dots, t_m) dt_1 \dots dt_m . \end{aligned} \quad (5.2.14)$$

Formula (5.2.4), or more precisely, the formula

$$A_1 = G_{1,2} h^2 + \frac{1}{2} G_{1,23} h^2 h^3 + \dots \quad (5.2.15)$$

and other main formulas remain invariant when we transform to the spectral representation or perform other transformations (5.2.9). If (5.2.15) is written out in detail, we have

$$\begin{aligned} A_\alpha(\omega_1) &= \int G_{\alpha,\beta}(\omega_1; \omega_2) h^\beta(\omega_2) d\omega_2 \\ &+ \frac{1}{2} \int G_{\alpha,\beta\gamma}(\omega_1; \omega_2, \omega_3) h^\beta(\omega_2) h^\gamma(\omega_3) d\omega_2 d\omega_3 + \dots \end{aligned} \quad (5.2.16)$$

in the spectral representation. According to (5.2.13), a spectral form of the contravariant tensor, say, $Q^{1,2}$ is given by

$$Q^{1,2} = (2\pi)^{-1} \int \exp(i\omega_1 t_1 + i\omega_2 t_2) Q^{\alpha_1, \alpha_2}(t_1, t_2) dt_1 dt_2. \quad (5.2.17)$$

It is well known that the superscript can be lowered by using the metric tensor g_{12} :

$$h_1 = g_{12} h^2, \quad (5.2.18a)$$

$$Q_{12} = g_{13} g_{24} Q^{34}. \quad (5.2.18b)$$

In the spectral representations (5.2.11, 13) the tensor

$$g_{12} = \delta_{\alpha_1 \alpha_2} \delta(\omega_1 + \omega_2), \quad (5.2.19)$$

i.e. the operator that changes the sign of the frequency, in other words, the complex conjugation operator, plays the role of the metric tensor. In fact, if we interchange the signs of the frequency on the right-hand side of (5.2.13), we obtain the transformation analogous to (5.2.11), and (5.2.17) goes over to

$$Q_{1,2} = (2\pi)^{-1} \int \exp(-i\omega_1 t_1 - i\omega_2 t_2) Q_{\alpha_1, \alpha_2}(t_1, t_2) dt_1 dt_2 \quad (5.2.20)$$

which is of the type (5.2.14).

Since in the time representation $G_{1,2\dots m}$ (and $Q_{1,2\dots m}$) depends only on the time differences $t_k - t_l \equiv t_{kl}$, the spectrum (5.2.14) assumes the form

$$G_{\alpha_1, \alpha_2 \dots \alpha_m}(\omega_1, \dots, \omega_m) = G'_{\alpha_1, \alpha_2 \dots \alpha_m}(\omega_1, \dots, \omega_{m-1}) \delta(\omega_1 + \dots + \omega_m), \quad (5.2.21)$$

where

$$\begin{aligned} G'_{\alpha_1, \alpha_2 \dots \alpha_m}(\omega_1, \dots, \omega_{m-1}) &= (2\pi)^{1-m/2} \int \exp(-i\omega_1 t_{1m} - \dots - i\omega_{m-1} t_{m-1,m}) \\ &\times G_{\alpha_1, \alpha_2 \dots \alpha_m}(t_1, \dots, t_m) dt_{1m} \dots dt_{m-1,m}. \end{aligned} \quad (5.2.22)$$

The admittance $G_{1,2\dots m}$ can be represented as

$$\begin{aligned} G_{\alpha_1, \alpha_2 \dots \alpha_m}(t_1, \dots, t_m) &= P_{2\dots m} G_{\alpha_1, \alpha_2 \dots \alpha_m}(t_1, \dots, t_m) \eta(t_1, \dots, t_m), \end{aligned} \quad (5.2.23)$$

where $P_{2 \dots m}$ means the summation over all permutations of the subscripts $2, \dots, m$, the number of the permutations being equal to $(m - 1)!$, where

$$\begin{aligned}\eta(t_1, \dots, t_m) &= \eta(t_{12})\eta(t_{23}) \dots \eta(t_{m-1,m}), \\ \eta(t) = g(t) &= 1 \quad \text{for } t > 0, \\ \eta(t) = g(t) &= 0 \quad \text{for } t < 0.\end{aligned}\tag{5.2.24}$$

Hence (5.2.21) can be written as

$$\begin{aligned}G_{\alpha_1, \alpha_2 \dots \alpha_m}(\omega_1, \dots, \omega_m) \\ = P_{2 \dots m} g'_{\alpha_1, \alpha_2 \dots \alpha_m}(\omega_1, \dots, \omega_{m-1}) \delta(\omega_1 + \dots + \omega_m),\end{aligned}\tag{5.2.25}$$

where

$$\begin{aligned}g'_{\alpha_1, \alpha_2 \dots \alpha_m}(\omega_1, \dots, \omega_{m-1}) \\ = (2\pi)^{1-m/2} \int \exp(-i\omega_1 t_{1m} - \dots - i\omega_{m-1} t_{m-1,m}). \\ \times G_{\alpha_1, \alpha_2 \dots \alpha_m}(t_1, \dots, t_m) \eta(t_1, \dots, t_m) dt_{1m} \dots dt_{m-1,m}.\end{aligned}\tag{5.2.26}$$

Analogously, from (5.2.20) we have

$$Q_{1,2} = q'_{\alpha_1, \alpha_2}(\omega_1) \delta(\omega_1 + \omega_2),\tag{5.2.27}$$

where

$$q'_{\alpha_1, \alpha_2}(\omega_1) = \int \exp(-i\omega_1 t_{12}) Q_{\alpha_1, \alpha_2}(t_1, t_2) dt_{12}.\tag{5.2.28}$$

If we use (5.2.18b), from (5.2.27) we obtain the form of the contravariant tensor in the spectral representation

$$Q^{1,2} = q'_{\alpha_1, \alpha_2}(-\omega_1) \delta(\omega_1 + \omega_2).\tag{5.2.29}$$

The functions (5.2.26) in (5.2.25) and the analogous functions for the modified admittances and impedances satisfy the Kramers–Kronig relations with respect to each of the variables $\omega'_i = \sum_{j=1}^i \omega_j$, $i = 1, \dots, m - 1$. These relations are derived by the same method used in the linear theory. The above dependence of ω'_i on ω_j is obtained by representing the integral on the right-hand side of (5.2.26) in the form

$$\begin{aligned}\int \exp(-i\omega'_1 t_{12} - i\omega'_2 t_{23} - \dots - i\omega'_{m-1} t_{m-1,m}) \eta(t_{12}) \eta(t_{23}) \\ \times \dots \eta(t_{m-1,m}) G_{\alpha_1, \alpha_2, \dots, \alpha_m}(t_1, \dots, t_m) dt_{12} dt_{23} \dots dt_{m-1,m}.\end{aligned}\tag{5.2.30}$$

Relationships of the Kramers–Kronig type are not used in this book and therefore, we shall not write them down or prove them.

5.2.3 Passing to the Quantum Case

Until now we have considered the nonquantum case. For generality we will now carry out the study at the quantum level using the concepts and formulas of the

quantum theory. As is generally known, quantum results yield the nonquantum results when Planck's constant tends to zero.

In quantum theory noncommuting objects, i.e. operators, play the role of the dynamical variables and the functions of these variables. For this reason the internal parameters $B_\alpha = B_\alpha(z)$ should now be regarded as the operators \hat{B}_α (in the beginning we denote a quantum operator by “ $\hat{}$ ”). Their averages

$$A_\alpha = \langle \hat{B}_\alpha \rangle = \text{Tr} \{ \hat{B}_\alpha \hat{\rho} \} \quad (5.2.31)$$

have the ordinary numerical character (they are *C*-numbers). Instead of (5.2.1), in the quantum case we have

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_0 - \sum_{\alpha=1}^r \hat{B}_\alpha h_\alpha(t) . \quad (5.2.32)$$

The external forces $h_\alpha(t)$ are *C*-numbers.

When we go over to the quantum case, equations (5.2.2–8) do not change.

The Hamiltonian (5.2.32) determines the time evolution of operators in the Heisenberg representation. In the Schrödinger representation the operators \hat{B}_α and the other operators of the dynamic type remain unchanged; the exception is the matrix $\hat{\rho}$ in (5.2.31), which varies in time. This matrix satisfies the quantum Liouville equation

$$\frac{d\hat{\rho}(t)}{dt} = -\frac{i}{\hbar} \{ \hat{\mathcal{H}}(t) \hat{\rho}(t) - \hat{\rho}(t) \hat{\mathcal{H}}(t) \} \equiv -\frac{i}{\hbar} [\hat{\mathcal{H}}(t), \hat{\rho}(t)] . \quad (5.2.33)$$

The solution of this equation is the density matrix

$$\hat{\rho}(t) = \hat{U}_{t_0 t} \hat{\rho}(t_0) \hat{U}_{t_0 t}^\dagger, \quad t > t_0 , \quad (5.2.34)$$

evolving from its initial value $\hat{\rho}(t_0)$, where $\hat{U}_{t_0 t}$ is the family of matrices satisfying the equation

$$\frac{d}{dt} \hat{U}_{t_0 t} = -\frac{i}{\hbar} \hat{\mathcal{H}}(t) \hat{U}_{t_0 t}, \quad t > t_0 , \quad (5.2.35)$$

under the initial conditions $\hat{U}_{t_0 t_0} = \hat{I}$ (\hat{I} is the identity operator). The above matrices are unitary:

$$\hat{U}_{t_0 t} \equiv \hat{U}_{t_0 t}^{-1} = \hat{U}_{t_0 t}^\dagger \quad (5.2.36)$$

(the superscript “ \dagger ” means the Hermitian conjugate).

The operators depending on time

$$\hat{D}(t) = \hat{U}_{t_0 t} \hat{D} \hat{U}_{t_0 t}^\dagger, \quad t > t_0 \quad (5.2.37)$$

correspond to the Heisenberg representation where the density matrix $\hat{\rho}$ is independent of time. We have

$$\langle \hat{D}(t) \rangle = \text{Tr} \{ \hat{D}(t) \hat{\rho}(t_0) \} = \text{Tr} \{ \hat{D} \hat{\rho}(t) \} . \quad (5.2.38)$$

Hence the means are identical in both representations.

Let us now introduce the operators

$$\hat{V}_{t_0} = \exp \left[\frac{i}{\hbar} \hat{\mathcal{H}}_0(t - t_0) \right] \hat{U}_{t_0}, \quad t > t_0. \quad (5.2.39)$$

On differentiating (5.2.39) and using (5.2.35), we get

$$\frac{d}{dt} \hat{V}_{t_0} = \exp \left[\frac{i}{\hbar} \hat{\mathcal{H}}_0(t - t_0) \right] \left\{ \frac{i}{\hbar} \hat{\mathcal{H}}_0 - \frac{i}{\hbar} \hat{\mathcal{H}}(t) \right\} \hat{U}_{t_0}. \quad (5.2.40)$$

Substituting (5.2.32) into (5.2.40) and introducing the definition

$$\hat{B}_\alpha^0(t) = \exp \left[\frac{i}{\hbar} \hat{\mathcal{H}}_0(t - t_0) \right] \hat{B}_\alpha \exp \left[- \frac{i}{\hbar} \hat{\mathcal{H}}_0(t - t_0) \right], \quad (5.2.41)$$

we obtain

$$\frac{d}{dt} \hat{V}_{t_0} = \frac{i}{\hbar} \hat{B}_\alpha^0(t) h_\alpha(t) \hat{V}_{t_0}. \quad (5.2.42)$$

Solving (5.2.39) for U_{t_0} and substituting the result into (5.2.37), we arrive at

$$\hat{D}(t) = \hat{V}_{t_0} \hat{D}^0(t) \hat{V}_{t_0}, \quad (5.2.43)$$

where $\hat{D}^0(t)$ is determined by analogy with (5.2.41). It is essential that the operators $\hat{D}^0(t)$ and $\hat{B}^0(t)$ are both independent of the external forces $h(t)$; only operators of the type (5.2.43) depend on these forces.

Under the initial condition $\hat{V}_{t_0 t_0} = \hat{I}$, the solution of (5.2.42) can be written in the form of a time-ordered exponent:

$$\hat{V}_{t_0} = \overleftarrow{\exp} \left[\frac{i}{\hbar} \int_{t_0}^t \hat{B}^0(t') h(t') dt' \right], \quad t \geq t_0. \quad (5.2.44)$$

The unitary condition $\hat{V}_{t_0 t} = \hat{V}_{t_0}^\dagger$, which is analogous to (5.2.36), can be easily verified. The arrow above the exponent in (5.2.44) indicates the principle of ordering of the operators $\hat{B}^0(t')$: the larger the time t' , the more to the left the corresponding operator $\hat{B}^0(t')$ stands. The ordered exponent can also be written in the form of a limit

$$\hat{V}_{t_0} = \lim_{n \rightarrow \infty} [\hat{I} + \hat{L}(t_{n-1}) \Delta] [\hat{I} + \hat{L}(t_{n-2}) \Delta] \dots [\hat{I} + \hat{L}(t_1) \Delta] [\hat{I} + \hat{L}(t_0) \Delta], \quad (5.2.45)$$

where

$$\Delta = (t - t_0)/n, \quad t_j = t_0 + j\Delta, \quad \hat{L}(t_j) = (i/\hbar) \hat{B}^0(t_j) h(t_j). \quad (5.2.46)$$

5.2.4 Formulas for Functional Derivatives with Respect to External Forces

Differentiation of (5.2.44) with respect to $h(t_1)$ gives

$$\frac{\delta \hat{V}_{t_0}}{\delta h_{\alpha_1}(t_1)} = \hat{V}_{t_1} \frac{i}{\hbar} \hat{B}_{\alpha_1}^0(t_1) \hat{V}_{t_1 t_0}, \quad t_0 < t_1 < t. \quad (5.2.47)$$

It is easy to check the validity of this expression by using (5.2.45). Using (5.2.47), we

find the functional derivative of the Heisenberg operator (5.2.43):

$$\frac{\delta \hat{D}(t)}{\delta h_1} = \frac{i}{\hbar} \{ \hat{V}_{t_0 t} \hat{D}^0(t) \hat{V}_{t_1} \hat{B}_1 \hat{V}_{t_1 t_0} - \hat{V}_{t_0 t_1} \hat{B}_1^0 \hat{V}_{t_1 t} \hat{D}^0 \hat{V}_{t_0} \}. \quad (5.2.48)$$

Substituting $\hat{V}_{t_1} = \hat{V}_{t_0} \hat{V}_{t_0 t_1}$ and $\hat{V}_{t_1 t} = \hat{V}_{t_1 t_0} \hat{V}_{t_0 t}$ into (5.2.48) and using a formula of the type (5.2.43), we obtain

$$\frac{\delta \hat{D}(t)}{\delta h_1} = \frac{i}{\hbar} (\hat{D}(t) \hat{B}_1 - \hat{B}_1 \hat{D}(t)) \equiv \frac{i}{\hbar} [\hat{D}(t), \hat{B}_{\alpha_1}(t_1)], \quad \text{for } t > t_1. \quad (5.2.49)$$

We have the complete Heisenberg operators on the right-hand side of (5.2.49). The value of t_0 should be set equal to $-\infty$. Since $\delta \hat{D}(t)/\delta h_1 = 0$ for $t_1 > t$, we can write the equation

$$\frac{\delta \hat{D}(t)}{\delta h_1} = \frac{i}{\hbar} [\hat{D}(t), \hat{B}_1] \eta(t - t_1), \quad (5.2.50)$$

which is valid everywhere. Here $\eta(\tau)$ is the unit step function coinciding with (5.1.44). Let us now find $\delta^{m-1} \hat{B}_1 / \delta h_2 \dots \delta h_m$. We suppose that the time instants t_1, t_2, \dots, t_m are ordered as follows: $t_1 > t_2 > t_3 > \dots > t_m$. Differentiating with respect to h_m , which corresponds to the earliest instant of time t_m , and applying (5.2.49) for $\hat{D} \rightarrow \hat{B}_1$, $\hat{B}_1 \rightarrow \hat{B}_m$, we arrive at

$$\frac{\delta \hat{B}_1}{\delta h_m} = \frac{i}{\hbar} [\hat{B}_1, \hat{B}_m]. \quad (5.2.51)$$

We now differentiate (5.2.51) with respect to h_{m-1} . Due to the law of causality \hat{B}_m is independent of h_{m-1} for $t_{m-1} > t_m$. Hence, the differentiation can be performed in the following way:

$$\frac{\delta^2 \hat{B}_1}{\delta h_{m-1} \delta h_m} = \frac{i}{\hbar} \left[\frac{\delta \hat{B}_1}{\delta h_{m-1}}, \hat{B}_m \right]. \quad (5.2.52)$$

Applying (5.2.49) once more gives

$$\frac{\delta^2 \hat{B}_1}{\delta h_{m-1} \delta h_m} = \left(\frac{i}{\hbar} \right)^2 [[\hat{B}_1, \hat{B}_{m-1}], \hat{B}_m]. \quad (5.2.53)$$

Then we differentiate (5.2.53) with respect to h_{m-2} , etc. Finally, we shall differentiate the equation determining $\delta^{m-2} \hat{B}_1 / \delta h_3 \dots \delta h_m$ with respect to h_2 , i.e. with respect to forces corresponding to the latest of the instants t_2, t_3, \dots, t_m . While doing so, the derivative can be put inside all the commutation brackets, and equation (5.2.49) can be applied with h_2 instead of h_1 . As a result we obtain

$$\frac{\delta^{m-1} \hat{B}_1}{\delta h_2 \dots \delta h_m} = \left(\frac{i}{\hbar} \right)^{m-1} [\dots [[\hat{B}_1, \hat{B}_2], \hat{B}_3], \dots, \hat{B}_m] \quad (5.2.54)$$

for $t_1 > t_2 > \dots > t_m$.

We note that the differentiation in (5.2.54) can be performed in the reverse order.

Using the function

$$\begin{aligned}\eta_{12\dots m} &= \eta(t_1, \dots, t_m) = \eta(t_{12})\eta(t_{23})\dots\eta(t_{m-1,m}) \\ &= \begin{cases} 1 & \text{for } t_1 > t_2 > \dots > t_m \\ 0 & \text{elsewhere,} \end{cases} \quad (5.2.55)\end{aligned}$$

we define

$$g_{12\dots m} = G_{1,2\dots m} \eta_{12\dots m}. \quad (5.2.56)$$

Substituting (5.2.3), i.e.

$$G_{1,2\dots m} = \left\langle \frac{\delta^{m-1} \hat{B}_1}{\delta h_2 \dots \delta h_m} \right\rangle_{h \equiv 0}, \quad (5.2.57)$$

into (5.2.56) and using (5.2.54), we find

$$g_{1,2\dots m} = (i/\hbar)^{m-1} \langle [\dots [[\hat{B}_1, \hat{B}_2], \hat{B}_3], \dots, \hat{B}_m] \rangle_0 \eta_{12\dots m}. \quad (5.2.58)$$

Thus, we have found (5.2.56), i.e. we have expressed it in terms of commutators. In order to find the complete admittance $G_{1,2\dots m}$, we should use its symmetry properties of the type (5.2.5) and causality properties (5.2.6). Denoting

$$V_{12\dots m} = \langle [\dots [[\hat{B}_1, \hat{B}_2], \hat{B}_3], \dots, \hat{B}_m] \rangle_{h \equiv 0}. \quad (5.2.59)$$

We have the general formula

$$G_{1,2\dots m} = P_{2\dots m} (i/\hbar)^{m-1} V_{12\dots m} \eta_{12\dots m} \text{ at } h \equiv 0. \quad (5.2.60)$$

Here $P_{2\dots m}$ has the same sense as in (5.2.25). We can now substitute (5.2.29) into (5.2.60). Formula (5.2.60) was obtained by *Bernard* and *Callen* [5.2].

5.2.5 Formula for Permutation of Operators Under Averaging Sign in the Absence of External Forces

Let the derivatives in Sect. 5.2.4 now be taken at the zero point $h(t) \equiv 0$. Then the mean values corresponding to zero external forces appear on the right-hand sides of (5.2.59, 60). We suppose that the system under consideration has evolved for an infinitely long time so that all its “initial nonequilibrium effects” have been attenuated. The nonequilibrium properties of the process $\hat{B}(t)$ are therefore caused only by the external forces $h(t)$; the process $\hat{B}(t)$ is an equilibrium process when the external forces are equal to zero. Consequently, the equilibrium values of the commutators appear in (5.2.59, 60). We now note that at $h(t) = 0$, the Heisenberg operators (5.2.43) coincide with the operators of the type (5.2.41), which are marked with the superscript “0”. We can therefore, write $\hat{B}_\alpha^0(t)$ instead of $\hat{B}_\alpha(t)$ on the right-hand side of (5.2.58).

The equilibrium mean value

$$\langle \hat{M}(t) \rangle_{h \equiv 0} = \langle \hat{M}^0(t) \rangle_0 = \text{Tr} \{ \hat{M}^0(t) \hat{\rho}_0 \} \quad (5.2.61)$$

is taken with the equilibrium density matrix $\hat{\rho}_0$. In the energy version we should

take the quantum Gibbs density matrix

$$\hat{\rho}_0 = \exp[(F - \hat{\mathcal{H}}_0)/kT] \quad (5.2.62)$$

as the equilibrium density matrix. Formula (5.2.62) is the quantum analogue of (2.2.5). Let us consider the equilibrium average of the product of two operators:

$$\langle \hat{Q}\hat{D}^0 \rangle_0 = \text{Tr}\{\hat{Q}\hat{D}^0(t)\hat{\rho}_0\}. \quad (5.2.63)$$

Let one of the averaged operators depend on time according to a formula of the type (5.2.41), i.e.

$$\hat{D}^0(t) = \exp\left[\frac{i}{\hbar}\hat{\mathcal{H}}_0(t - t_0)\right]\hat{D}(t_0)\exp\left[-\frac{i}{\hbar}\hat{\mathcal{H}}_0(t - t_0)\right]. \quad (5.2.64)$$

Since the trace has the property

$$\text{Tr}\{\hat{Q}\hat{M}\} = \text{Tr}\{\hat{M}\hat{Q}\}, \quad (5.2.65)$$

equation (5.2.63) can be written in the form

$$\langle \hat{Q}\hat{D}^0(t) \rangle_0 \equiv \text{Tr}\{\hat{Q}\hat{D}^0(t)\hat{\rho}_0\} = \text{Tr}\{\hat{D}^0(t)\hat{\rho}_0\hat{Q}\}, \quad (\hat{M} = \hat{D}^0\hat{\rho}_0). \quad (5.2.66)$$

Substituting (5.2.62) into (5.2.66), we readily verify that the latter can be written as

$$\langle \hat{Q}\hat{D}^0(t) \rangle_0 = \text{Tr}\{\hat{\rho}_0\hat{\rho}_0^{-1}\hat{D}^0(t)\hat{\rho}_0\hat{Q}\} = \langle \hat{D}^0(t)\hat{Q} \rangle_0, \quad (5.2.67)$$

where

$$\hat{D}^0(t) = \hat{\rho}_0^{-1}\hat{D}^0\hat{\rho}_0 = \exp(\beta\hat{\mathcal{H}}_0)\hat{D}_0\exp(-\beta\hat{\mathcal{H}}_0) \quad (\beta^{-1} = kT). \quad (5.2.68)$$

Using (5.2.64), it is easy to see that (5.2.68) can be written in the form

$$\hat{D}^0(t) = \hat{D}^0(t - i\hbar\beta). \quad (5.2.69)$$

Expanding $\hat{D}^0(t - i\hbar\beta)$ in a Taylor series, we arrive at

$$\hat{D}^0(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial^n \hat{D}^0(t)}{\partial t^n} (-i\hbar\beta)^n \equiv \exp(-i\hbar\beta p_D) \hat{D}^0(t). \quad (5.2.70)$$

Here $p_D = \partial/\partial t$ is the differentiation operator related to $\hat{D}^0(t)$. Substituting (5.2.70) into (5.2.67), we obtain the formula

$$\langle \hat{Q}\hat{D}^0(t) \rangle_0 = \exp(-i\hbar\beta p_D) \langle \hat{D}^0(t)\hat{Q} \rangle_0, \quad (5.2.71)$$

which will be used later.

5.2.6 Consequences of Formula (5.2.71)

1. Subtraction of $\langle \hat{D}^0(t)\hat{Q} \rangle_0$ from both sides of equation (5.2.71) gives

$$\langle [\hat{Q}, \hat{D}(t)] \rangle_0 = [\exp(-i\hbar\beta p_D) - 1] \langle \hat{D}(t)\hat{Q} \rangle_0. \quad (5.2.72)$$

For brevity, we omit here and subsequently the superscripts “0”. If this equation is rearranged to solve for $\langle \hat{D}(t)\hat{Q} \rangle_0$, we obtain

$$\langle \hat{D}(t)\hat{Q} \rangle_0 = -\Gamma^+(p_D) \langle [\hat{Q}, \hat{D}(t)] \rangle_0, \quad (5.2.73)$$

where we have defined

$$\Gamma^+(p) = \exp(i\hbar\beta p)/[\exp(i\hbar\beta p) - 1]. \quad (5.2.74)$$

It should be noted that the moment $\langle \hat{D}(t)\hat{Q} \rangle_0$ is not quite uniquely determined by (5.2.73). To the right-hand side of (5.2.73) one can add a constant, i.e. a quantity independent of t :

$$\langle \hat{D}(t)\hat{Q} \rangle_0 = \Gamma^+(p_D)\langle [\hat{D}(t), \hat{Q}] \rangle_0 + \text{const.} \quad (5.2.75)$$

In fact, by letting the operator $\exp(-i\hbar\beta p_D) - 1$ act on both sides of (5.2.75), we obtain (5.2.72) since

$$[\exp(-i\hbar\beta p_D) - 1] \text{const.} = 0. \quad (5.2.76)$$

The product $\langle \hat{D}(t) \rangle_0 \langle \hat{Q} \rangle_0$ is independent of t . Therefore, instead of (5.2.73) we may just as well take for the correlator the formula

$$\langle \hat{D}(t), \hat{Q} \rangle_0 = \Gamma^+(p_D)\langle [\hat{D}(t), \hat{Q}] \rangle_0. \quad (5.2.77)$$

If we set $\hat{Q} = \hat{B}$ in (5.2.73), we have

$$\langle \hat{D}\hat{B} \rangle_0 = \Gamma_D^+ \langle [\hat{D}, \hat{B}] \rangle_0 \quad (5.2.78a)$$

$$\langle \hat{B}\hat{D} \rangle_0 = \Gamma_D^- \langle [\hat{D}, \hat{B}] \rangle_0 \quad (5.2.78b)$$

where

$$\Gamma_D^+ = \Gamma^+(p_D), \quad \Gamma_D^- = \Gamma_D^+ - 1 = [\exp(i\hbar\beta p_D) - 1]^{-1}. \quad (5.2.79)$$

2. We now consider $\langle \hat{D}\hat{B}_1\hat{B}_2 \rangle_0$. Applying (5.2.78a), where \hat{B} is replaced by $\hat{B}_1\hat{B}_2$, we find

$$\langle \hat{D}\hat{B}_1\hat{B}_2 \rangle_0 = \Gamma_D^+ \langle [\hat{D}, \hat{B}_1\hat{B}_2] \rangle_0. \quad (5.2.80)$$

It is easy to verify that the commutation brackets have the distributive property, i.e.

$$[\hat{D}, \hat{B}_1\hat{B}_2] = [\hat{D}, \hat{B}_1]\hat{B}_2 + \hat{B}_1[\hat{D}, \hat{B}_2]. \quad (5.2.81)$$

Using this, we obtain from (5.2.80)

$$\langle \hat{D}\hat{B}_1\hat{B}_2 \rangle_0 = \Gamma_D^+ \{ \langle [\hat{D}, \hat{B}_1]\hat{B}_2 \rangle_0 + \langle \hat{B}_1[\hat{D}, \hat{B}_2] \rangle_0 \}. \quad (5.2.82)$$

Turning to the average $\langle \hat{B}_1\hat{D}\hat{B}_2 \rangle$, we have

$$\langle \hat{B}_1\hat{D}\hat{B}_2 \rangle_0 = \langle \hat{D}\hat{B}_1\hat{B}_2 \rangle_0 - \langle [\hat{D}, \hat{B}_1]\hat{B}_2 \rangle_0. \quad (5.2.83)$$

If we substitute (5.2.82) into (5.2.83) and use (5.2.79), we find

$$\langle \hat{B}_1\hat{D}\hat{B}_2 \rangle_0 = \Gamma_D^- \langle [\hat{D}, \hat{B}_1]\hat{B}_2 \rangle_0 + \Gamma_D^+ \langle \hat{B}_1[\hat{D}, \hat{B}_2] \rangle_0. \quad (5.2.84)$$

Finally, we take the average $\langle \hat{B}_1\hat{B}_2\hat{D} \rangle$. Employing (5.2.78b) with $\hat{B} = \hat{B}_1\hat{B}_2$ and taking into account the distributive property, we arrive at

$$\langle \hat{B}_1\hat{B}_2\hat{D} \rangle_0 = \Gamma_D^- \{ \langle [\hat{D}, \hat{B}_1]\hat{B}_2 \rangle_0 + \langle \hat{B}_1[\hat{D}, \hat{B}_2] \rangle_0 \}_0. \quad (5.2.85)$$

We now introduce the repeated commutators into (5.2.82, 84, 85). We transform the term $\langle [\hat{D}, \hat{B}_1]\hat{B}_2 \rangle_0$ in (5.2.82) using formula (5.2.78a) in which $[\hat{D}, \hat{B}_1]$ and \hat{B}_2 are

substituted for \hat{D} and \hat{B} , respectively. The term $\langle \hat{B}_1 [\hat{D}, \hat{B}_2] \rangle_0$ is transformed by using formula (5.2.78b) in which $[\hat{D}, \hat{B}_2]$ and \hat{B}_1 are substituted for \hat{D} and \hat{B} , respectively. As a result, (5.2.82) takes the form

$$\langle \hat{D} \hat{B}_1 \hat{B}_2 \rangle_0 = \Gamma_D^+ \{ \Gamma_{D1}^+ \langle [[\hat{D}, \hat{B}_1], \hat{B}_2] \rangle_0 + \Gamma_{D2}^- \langle [[\hat{D}, \hat{B}_2], \hat{B}_1] \rangle_0 \}, \quad (5.2.86)$$

where

$$\Gamma_{D1}^+ = \Gamma^+ (p_D + p_1), \quad \Gamma_{D2}^- = \Gamma^- (p_D + p_2). \quad (5.2.87)$$

Using (5.2.78), we can analogously transform (5.2.84) and obtain

$$\langle \hat{B}_1 \hat{D} \hat{B}_2 \rangle_0 = \Gamma_D^- \Gamma_{D1}^+ \langle [[\hat{D}, \hat{B}_1], \hat{B}_2] \rangle_0 + \Gamma_D^+ \Gamma_{D2}^- \langle [[\hat{D}, \hat{B}_2], \hat{B}_1] \rangle_0. \quad (5.2.88)$$

Equation (5.2.85) leads to

$$\langle \hat{B}_1 \hat{B}_2 \hat{D} \rangle_0 = \Gamma_D^- \{ \Gamma_{D1}^+ \langle [[\hat{D}, \hat{B}_1], \hat{B}_2] \rangle_0 + \Gamma_{D2}^- \langle [[\hat{D}, \hat{B}_2], \hat{B}_1] \rangle_0 \}. \quad (5.2.89)$$

3. We now proceed to the consideration of the equilibrium average of the product $\hat{B}_1 \hat{B}_2 \hat{B}_3 \hat{B}_4$. Setting $\hat{D} = \hat{B}_1$ and $\hat{B} = \hat{B}_2 \hat{B}_3 \hat{B}_4$ and using (5.2.78a), we find

$$\langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \hat{B}_4 \rangle_0 = \Gamma_1^+ \langle [\hat{B}_1, \hat{B}_2 \hat{B}_3 \hat{B}_4] \rangle_0, \quad (\Gamma_1^+ = \Gamma^+ (p_1)) \quad (5.2.90)$$

or, if we use the distributive property,

$$\begin{aligned} \langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \hat{B}_4 \rangle_0 &= \Gamma_1^+ \{ \langle [\hat{B}_1, \hat{B}_2] \hat{B}_3 \hat{B}_4 \rangle_0 + \langle \hat{B}_2 [\hat{B}_1, \hat{B}_3] \hat{B}_4 \rangle_0 \\ &\quad + \langle \hat{B}_2 \hat{B}_3 [\hat{B}_1, \hat{B}_4] \rangle_0 \}. \end{aligned} \quad (5.2.91)$$

We transform the first term in braces using formula (5.2.86) in which \hat{D} , \hat{B}_1 and \hat{B}_2 are replaced by $[\hat{B}_1, \hat{B}_2]$, \hat{B}_3 and \hat{B}_4 , respectively. Setting $\hat{D} = [\hat{B}_1, \hat{B}_3]$, we transform the second term according to (5.2.88). The third term is transformed according to (5.2.89) with $\hat{D} = [\hat{B}_1, \hat{B}_4]$. We thus obtain

$$\begin{aligned} \langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \hat{B}_4 \rangle_0 &= \Gamma_1^+ (\Gamma_{12}^+ \Gamma_{123}^+ V_{1234} + \Gamma_{12}^+ \Gamma_{124}^- V_{1243} + \Gamma_{13}^- \Gamma_{132}^+ V_{1324} \\ &\quad + \Gamma_{13}^+ \Gamma_{134}^- V_{1342} + \Gamma_{14}^- \Gamma_{142}^+ V_{1423} + \Gamma_{14}^- \Gamma_{143}^- V_{1432}). \end{aligned} \quad (5.2.92)$$

Here, in analogy with (5.2.59), we have used the notation

$$V_{1234} = \langle [[[\hat{B}_1, \hat{B}_2], \hat{B}_3], \hat{B}_4] \rangle_0. \quad (5.2.93)$$

If in (5.2.86) we replace \hat{D} , \hat{B}_1 and \hat{B}_2 by \hat{B}_1 , \hat{B}_2 and \hat{B}_3 , respectively, we arrive at

$$\langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \rangle_0 = \Gamma_1^+ (\Gamma_{12}^+ V_{123} + \Gamma_{13}^- V_{132}), \quad (V_{123} = \langle [[\hat{B}_1, \hat{B}_2], \hat{B}_3] \rangle_0). \quad (5.2.94)$$

4. We now recall that the action of the operators Γ^\pm is accompanied by some uncertainty which leads to the appearance of a constant in (5.2.75). Let us take the first term in (5.2.94). Due to the presence of the operators Γ_1^+ and Γ_{12}^+ we can add to the right-hand side an arbitrary function $f(t_1, t_2, t_3)$, which satisfies the condition $(\Gamma_{12}^+)^{-1} (\Gamma_1^+)^{-1} f = 0$, i.e. by virtue of (5.2.74) $f(t_1, t_2, t_3)$ satisfies the equation $p_1(p_1 + p_2)f = 0$. In fact, by letting the operator $(\Gamma_1^+ \Gamma_{12}^+)^{-1}$ act on $\Gamma_1^+ \Gamma_{12}^+ V_{123} + f(t_1, t_2, t_3)$, we obtain V_{123} as we should.

The general form of the function that satisfies the equation $p_1(p_1 + p_2)f = 0$ is as follows:

$$f(t_1, t_2, t_3) = \varphi(t_2 - t_3) + \varphi'(t_1 - t_2) + \text{const.} \quad (5.2.95)$$

where φ and φ' are arbitrary functions. We have written $f(t_2 - t_3)$, and not $f(t_2, t_3)$ in view of the stationarity condition. The second term in (5.2.94) also leads to the addition of an arbitrary function $\varphi''(t_1 - t_3)$. As a result, we have the function

$$f(t_1, t_2, t_3) = \varphi(t_{23}) + \varphi'(t_{12}) + \varphi''(t_{13}) + \text{const.} \quad (5.2.96)$$

According to formula (2.1.14), written for the quantum case, the difference between the moment $\langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \rangle_0$ and the correlator $\langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle_0$ is equal to

$$\begin{aligned} \langle \hat{B}_1, \hat{B}_2 \rangle_0 \langle \hat{B}_3 \rangle_0 + \langle \hat{B}_1, \hat{B}_3 \rangle \langle \hat{B}_2 \rangle_0 + \langle \hat{B}_2, \hat{B}_3 \rangle_0 \langle \hat{B}_1 \rangle_0 \\ + \langle \hat{B}_1 \rangle_0 \langle \hat{B}_2 \rangle_0 \langle \hat{B}_3 \rangle_0. \end{aligned} \quad (5.2.97)$$

It belongs to the admissible class of arbitrary functions. For this reason, instead of (5.2.94) we can write an analogous formula for the correlator

$$\langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle_0 = \Gamma_1^+ (\Gamma_{12}^+ V_{123} + \Gamma_{13}^- V_{132}), \quad (5.2.98)$$

where the addition of arbitrary functions of the type $\varphi(t_{23}) + \varphi'(t_{12}) + \varphi''(t_{13}) + \text{const.}$ is implied.

We now proceed to consider equation (5.2.92) and take its first term $\Gamma_1^+ \Gamma_{12}^+ \Gamma_{123}^+ V_{1234}$. This term contains the arbitrary function f satisfying the condition

$$p_1(p_1 + p_2)(p_1 + p_2 + p_3)f(t_1, t_2, t_3, t_4) = 0, \quad (5.2.99)$$

i.e. $f = \varphi^{(1)} + \varphi^{(2)} + \varphi^{(3)}$, where $\varphi^{(j)}$ are functions satisfying the equations

$$\begin{aligned} p_1 \varphi^{(1)} = 0, \quad (p_1 + p_2) \varphi^{(2)} = 0, \\ (p_1 + p_2 + p_3) \varphi^{(3)} = -p_4 \varphi^{(3)} = 0, \quad (p_i = \partial/\partial t_i). \end{aligned} \quad (5.2.100)$$

Hence we obtain the following additive arbitrary function

$$f(t_1, t_2, t_3) = \varphi^{(1)}(t_{24}, t_{34}) + \varphi^{(2)}(t_{12}, t_{34}) + \varphi^{(3)}(t_{12}, t_{13}). \quad (5.2.101)$$

Here the stationary condition is used. The consideration of other terms in (5.2.92) leads to the possibility of adding other terms of the identical type in (5.2.101). The terms of the difference $\langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \hat{B}_4 \rangle_0 - \langle \hat{B}_1, \hat{B}_2, \hat{B}_3, \hat{B}_4 \rangle_0$ [see (2.1.15)] belong to the admissible class of functions. Therefore, we may just as well write the correlator on the left-hand side of (5.2.92) in the form

$$\begin{aligned} \langle \hat{B}_1, \hat{B}_2, \hat{B}_3, \hat{B}_4 \rangle_0 = \Gamma_1^+ (\Gamma_{12}^+ \Gamma_{123}^+ V_{1234} + \Gamma_{12}^+ \Gamma_{124}^- V_{1243} + \Gamma_{13}^- \Gamma_{132}^+ V_{1324} \\ + \Gamma_{13}^+ \Gamma_{134}^- V_{1342} + \Gamma_{14}^- \Gamma_{142}^+ V_{1423} + \Gamma_{14}^- \Gamma_{143}^- V_{1432}). \end{aligned} \quad (5.2.102)$$

5.2.7 Identities for Operators Γ^\pm

The operators Γ^\pm defined by (5.2.74, 79) are functions of the differentiation operator in the time representation. In the spectral representation, the differentiation

operator p is transformed into $i\omega$. In this case, Γ^\pm are the numerical factors $\Gamma^\pm(i\omega)$.

Let us derive several identities for Γ^\pm , which are valid in every representation and will be used subsequently. We obtain a simple identity if we replace p by $-p$ in (5.2.74) and consider (5.2.79). This yields

$$\Gamma^+(-p) = -\Gamma^-(p). \quad (5.2.103)$$

Formula (5.2.103) can also be written as $\Gamma_2^- + \Gamma_1^+ = 0$ for $p_1 + p_2 = 0$.

Using the definitions of operators Γ^\pm , one can directly verify that the identities

$$\Gamma_2^- \Gamma_3^- + \Gamma_1^+ \Gamma_3^- + \Gamma_1^+ \Gamma_2^+ = 0, \quad \text{for } p_1 + p_2 + p_3 = 0 \quad (5.2.104)$$

and

$$\begin{aligned} \Gamma_2^- \Gamma_3^- \Gamma_4^- + \Gamma_1^+ \Gamma_3^- \Gamma_4^- + \Gamma_1^+ \Gamma_2^+ \Gamma_4^- + \Gamma_1^+ \Gamma_2^+ \Gamma_3^+ &= 0, \\ \text{for } p_1 + p_2 + p_3 + p_4 &= 0 \end{aligned} \quad (5.2.105)$$

are valid. It is obvious that the structures of the last three identities are identical.

The easily verifiable equations

$$\Gamma_1^+ + \Gamma_2^- = \Gamma_1^- + \Gamma_2^+ = \Gamma_1 + \Gamma_2, \quad (5.2.106)$$

where $\Gamma = \Gamma^+ - 1/2$, are also useful sometimes.

We also have a further group of identities

$$\begin{aligned} \Gamma_{12}^-(\Gamma_1^+ + \Gamma_2^-) &= \Gamma_1^- \Gamma_2^-, \\ \Gamma_{12}^+(\Gamma_1^+ + \Gamma_2^-) &= \Gamma_1^+ \Gamma_2^+, \\ \Gamma_{12}^+ \Gamma_1^- + \Gamma_{12}^- \Gamma_2^+ &= \Gamma_1^- \Gamma_2^+. \end{aligned} \quad (5.2.107)$$

Using (5.2.107), we readily obtain

$$\Gamma_3^- \Gamma_4^- \Gamma_{24}^- - \Gamma_2^- \Gamma_3^- \Gamma_4^- = -\Gamma_3^- \Gamma_2^+ \Gamma_{24}^-, \quad (5.2.108a)$$

$$-\Gamma_1^+ \Gamma_2^+ \Gamma_{13}^+ + \Gamma_1^+ \Gamma_2^+ \Gamma_3^+ = \Gamma_2^+ \Gamma_3^- \Gamma_{13}^+. \quad (5.2.108b)$$

If $p_1 + p_2 + p_3 + p_4 = 0$, then $\Gamma_{13}^+ = -\Gamma_{24}^-$ by virtue of (5.2.103). Therefore, the expression on the right-hand side of (5.2.108a) is equal to expression on the right-hand side of (5.2.108b). Consequently, we can equate the left-hand side of (5.2.108a) to the left-hand side of (5.2.108b):

$$\Gamma_3^- \Gamma_4^- \Gamma_{24}^- = \Gamma_2^- \Gamma_3^- \Gamma_4^- + \Gamma_1^+ \Gamma_2^+ \Gamma_3^+ - \Gamma_1^+ \Gamma_2^+ \Gamma_{13}^+, \quad \text{for } p_1 + p_2 + p_3 + p_4 = 0. \quad (5.2.109)$$

If we use (5.2.105), we find

$$\Gamma_3^- \Gamma_4^- \Gamma_{24}^- = -\Gamma_1^+ (\Gamma_3^- \Gamma_4^- + \Gamma_2^+ \Gamma_4^- + \Gamma_2^+ \Gamma_{13}^+), \quad \text{for } p_1 + p_2 + p_3 + p_4 = 0. \quad (5.2.110)$$

Multiplying (5.2.110) by $\exp(i\hbar\beta p_4)$, we also get

$$\Gamma_3^- \Gamma_4^+ \Gamma_{24}^- = -\Gamma_1^+ (\Gamma_3^- \Gamma_4^+ + \Gamma_2^+ \Gamma_4^+ + \Gamma_2^- \Gamma_{13}^-), \quad \text{for } p_1 + p_2 + p_3 + p_4 = 0. \quad (5.2.111)$$

The above identities will be sufficient for deriving some results later.

5.3 Linear and Quadratic FDRs of the Second Kind

5.3.1 Linear Fluctuation–Dissipation Theorem (FDT)

Here we derive the formula relating the correlator $\langle \hat{B}_1, \hat{B}_2 \rangle_0$ to the linear admittance $G_{1,2}$. Using (5.2.78b) in the correlator version of the type (5.2.77) with $\hat{B} = \hat{B}_1$ and $\hat{D} = \hat{B}_2$, we obtain

$$\langle \hat{B}_1, \hat{B}_2 \rangle_0 = -\Gamma_2^- \langle [\hat{B}_1, \hat{B}_2] \rangle_0. \quad (5.3.1)$$

Equation $\eta_{12} + \eta_{21} = 1$ ($\eta_{12} = \eta(t_{12})$) implies the identity

$$\langle [\hat{B}_1, \hat{B}_2] \rangle_0 = a_{12} + b_{21}, \quad (5.3.2)$$

where

$$a_{12} = \langle [\hat{B}_1, \hat{B}_2] \rangle_0 \eta_{12}, \quad b_{21} = \langle [\hat{B}_1, \hat{B}_2] \rangle_0 \eta_{21}. \quad (5.3.3)$$

The functions a_{kl} , b_{kl} , which are nonzero only for $t_k > t_l$, will be called the partial functions. Since $[\hat{B}_1, \hat{B}_2] = -[\hat{B}_2, \hat{B}_1]$ from (5.3.3) we have $b_{21} = -a_{21}$. Equation (5.3.2) can therefore be written as

$$\langle [\hat{B}_1, \hat{B}_2] \rangle_0 = a_{12} - a_{21}. \quad (5.3.4)$$

Using (5.2.58) for $m = 2$, we have as a consequence of (5.3.3) $g_{12} = (i/\hbar)a_{12}$. If we take into account that $g_{12} = G_{1,2}$ [see (5.2.56, 6)], then $a_{12} = (\hbar/i)G_{1,2}$ and from (5.3.4) we obtain

$$\langle [\hat{B}_1, \hat{B}_2] \rangle_0 = \frac{\hbar}{i}(G_{1,2} - G_{2,1}). \quad (5.3.5)$$

Substitution of (5.3.5) into (5.3.1) gives

$$\langle \hat{B}_1, \hat{B}_2 \rangle_0 = i\hbar\Gamma_2^-(G_{1,2} - G_{2,1}). \quad (5.3.6)$$

If we write the analogous equation in which the subscripts 1 and 2 are interchanged

$$\langle \hat{B}_2, \hat{B}_1 \rangle_0 = i\hbar\Gamma_1^-(G_{2,1} - G_{1,2}) \quad (5.3.7)$$

and if we add (5.3.7) to (5.3.6), we obtain

$$\langle [\hat{B}_1, \hat{B}_2]_+ \rangle_0 = i\hbar(\Gamma_2^- - \Gamma_1^-)(G_{1,2} - G_{2,1}). \quad (5.3.8)$$

Due to the stationarity condition, the equilibrium correlator and the function $G_{1,2}$ depend only on the time difference $(t_1 - t_2)$. Therefore, $p_2 = -p_1$. Using (5.2.103), we have $\Gamma_2^+ = \Gamma^+(-p_1) = -\Gamma^-(p_1)$. Consequently, (5.3.8) takes the form

$$\frac{1}{2}\langle [\hat{B}_1, \hat{B}_2]_+ \rangle_0 = -i\hbar\Gamma_1(G_{1,2} - G_{2,1}) = i\hbar\Gamma_2(G_{1,2} - G_{2,1}), \quad (5.3.9)$$

where

$$\Gamma(p) = \frac{1}{2}[\Gamma^+(p) + \Gamma^-(p)] = \Gamma^+(p) - \frac{1}{2} = \frac{1}{2}\coth(\frac{1}{2}i\beta\hbar p) \quad (5.3.10)$$

[we use (5.2.74, 79)]. Equation (5.3.9) is one of the formulations of linear FDT established by *Callen* and *Welton* [5.3] (see also [5.4]). If \hbar tends to zero in (5.3.9), we obtain the nonquantum formula

$$\langle B_1, B_2 \rangle_0 = -kT p_1^{-1} (G_{1,2} - G_{2,1}) = kT p_2^{-1} [G_{\alpha_1, \alpha_2}(t_{12}) - G_{\alpha_2, \alpha_1}(t_{21})]. \quad (5.3.11)$$

The operator p_2^{-1} in (5.3.11) means, naturally, integration with respect to t_2 in the time representation. Let us make specific the limits of integration and the additive constant, i.e. the constant of integration implied in (5.3.11). On assuming that $G_{\alpha_1 \alpha_2}(t_{12}) \rightarrow 0$ and $\langle B_1, B_2 \rangle_0 \rightarrow 0$ for $t_{12} \rightarrow \infty$, we obtain

$$\langle B_{\alpha_1}(t_1), B_{\alpha_2}(t_2) \rangle_0 = kT \int_{-\infty}^{t_2} G_{\alpha_1, \alpha_2}(t_1 - t'_2) dt'_2, \quad t_1 > t_2. \quad (5.3.12)$$

Here we have used the fact that the term with $G_{\alpha_2, \alpha_1}(t'_2 - t_1)$ is of no consequence since it is equal to zero for $t'_2 < t_1$.

Taking into account that $p_1 = i\omega_1 \equiv i\omega = -i\omega_2$ in the spectral representation, (5.3.9) can be written as

$$S_{\alpha\beta}(\omega) = \frac{i\hbar}{2} \coth\left(\frac{\hbar\omega}{2kT}\right) [G'_{\alpha, \beta}(\omega) - G'^{*}_{\beta, \alpha}(\omega)], \quad (5.3.13)$$

where

$$S_{\alpha\beta}(\omega) = \frac{1}{2} \int \exp(-i\omega t_{12}) \langle [\hat{B}_\alpha(t_1), \hat{B}_\beta(t_2)]_+ \rangle_0 dt_{12}, \quad (5.3.14a)$$

$$G'_{\alpha, \beta}(\omega) = \int \exp(-i\omega t_{12}) G_{\alpha, \beta}(t_{12}) dt_{12}. \quad (5.3.14b)$$

The superscript * in (5.3.13) denotes complex conjugation. It has been supposed that A_α , h_α and consequently $G_{\alpha, \beta}(t_{12})$ are real.

To end this section we shall derive another form of the linear fluctuation-dissipation relation, namely, the form suggested by Kubo [5.5] in 1957. Letting the operator $(\Gamma_2^-)^{-1} = -(\Gamma_1^+)^{-1}$, which is equal to $-[1 - \exp(-i\beta\hbar p_1)]$ by virtue of (5.2.74), act on both sides of (5.3.6), we obtain

$$i\hbar(G_{1,2} - G_{2,1}) = -[1 - \exp(-i\beta\hbar p_1)] \langle \hat{B}_1, \hat{B}_2 \rangle_0. \quad (5.3.15)$$

Using the time representation, we consider the region $t_2 > t_1$, where $G_{1,2}$ is equal to zero. Considering this fact and the identity

$$p_1 \int_0^\beta d\lambda \exp(-i\lambda\hbar p_1) = (i\hbar)^{-1} [1 - \exp(-i\beta\hbar p_1)], \quad (5.3.16)$$

we arrive at

$$G_{2,1} = \int_0^\beta d\lambda \exp(-i\hbar\lambda p_1) \langle \dot{\hat{B}}_1, \hat{B}_2 \rangle_0. \quad (5.3.17)$$

Since $\exp(i\tau p_1) \hat{B}_1^0 = \exp(i\tau \hat{\mathcal{H}}_0/\hbar) \hat{B}_1^0 \exp(-i\tau \hat{\mathcal{H}}_0/\hbar)$ by virtue of the dynamic equation, (5.3.17) can be written as

$$G_{2,1} = \int_0^\beta d\lambda \langle e^{\lambda \hat{\mathcal{H}}} \dot{\hat{B}}_1 e^{-\lambda \hat{\mathcal{H}}} \hat{B}_2 \rangle_0, \quad \text{for } t_2 > t_1 \quad (5.3.18)$$

(here the moment has been substituted for the correlator since $\langle \hat{B}_1 \rangle_0 = 0$). Relation (5.3.18) is the Kubo formula. The expression on the right-hand side of (5.3.18) is nothing but the quasiclassical moment $p_1 M_{12}^q$ (see (1.1.61), Vol. 2) multiplied by β . For this reason, relation (5.3.18), which is analogous to the nonquantum relation $G_{2,1} = \beta \langle \dot{B}_1 B_2 \rangle$ for $t_2 > t_1$, is quite natural. In fact, the quasiclassical moments and the ordinary nonquantum moments always satisfy the same relations.

5.3.2 Symmetry of Quantum Moments and Correlators Under Time-Reversal Transformation

We first consider the sense in which one can understand the symmetry of the quantum theory apparatus under the time-reversal transformation. Let us take the well-known commutation relations between coordinates and momenta

$$\hat{q}_\alpha \hat{p}_\beta - \hat{p}_\beta \hat{q}_\alpha = i\hbar \delta_{\alpha\beta}. \quad (5.3.19)$$

These relations play a fundamental role in the quantum theory. When time is reversed, the coordinates do not change, but the momenta change in sign: $\hat{q}_\alpha \rightarrow \hat{q}_\alpha$, $\hat{p}_\alpha \rightarrow -\hat{p}_\alpha$. From (5.3.19) we therefore obtain on time reversal

$$-\hat{q}_\alpha \hat{p}_\beta + \hat{p}_\beta \hat{q}_\alpha = i\hbar \delta_{\alpha\beta}. \quad (5.3.20)$$

These equations differ essentially from (5.3.19). The difference between the forms of the basic relations for direct and reverse times is inadmissible. To correct the situation, the time reversal, $t \rightarrow \tilde{t} = -t$, and the sign change of p_α should be accompanied by the operation of complex conjugation of all operators. This means that under the time-reversal transformation, the operators \hat{q} and \hat{p} must be replaced by \hat{q}^* and $-\hat{p}^*$, respectively. Then, as is easily seen, (5.3.19) will be invariant under time reversal. According to the above procedure an arbitrary operator \hat{D} must transform as

$$\hat{D} \rightarrow \varepsilon_D \hat{D}^*, \quad (5.3.21)$$

for $t \rightarrow -t$, where $\varepsilon_D = 1$ for time-even \hat{D} , and $\varepsilon_D = -1$ for time-odd \hat{D} . When time is reversed, the density matrix is replaced by its complex conjugate: $\hat{\rho} \rightarrow \hat{\rho}^*$. In the case when $\hat{\mathcal{H}}$ is independent of time, on setting $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0$, $\hat{D}(t) = \hat{B}^0(t)$ in (5.2.41), it follows that in the Heisenberg representation, the time dependence of \hat{D} is given by the dynamic equation

$$d\hat{D}(t)/dt = (i/\hbar)(\hat{\mathcal{H}}\hat{D}(t) - \hat{D}(t)\hat{\mathcal{H}}). \quad (5.3.22)$$

Performing the complex conjugation and setting $\tilde{t} = -t$, we find from (5.3.22)

$$d\hat{D}^*/d\tilde{t} = (i/\hbar)(\hat{\mathcal{H}}^*\hat{D}^* - \hat{D}^*\hat{\mathcal{H}}^*). \quad (5.3.23)$$

We demand that the time-reversed dynamic equation

$$d\hat{\tilde{D}}/d\tilde{t} = i/\hbar(\hat{\mathcal{H}}\hat{\tilde{D}} - \hat{\tilde{D}}\hat{\mathcal{H}}) \quad (5.3.24)$$

be of the same form as (5.3.22). The substitution of $\hat{\tilde{D}} = \varepsilon_D \hat{D}^*$ into (5.3.24) and comparison of the result with (5.3.23) yields

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^*. \quad (5.3.25)$$

As is shown below the condition of time reversibility can be written as

$$H_1(q, -p) = H_1(q, p), \quad (H_1(\hat{q}, \hat{p})^{(s)} = \hat{\mathcal{H}}). \quad (5.3.26)$$

In this case the dynamic equations are invariant under time reversal, and the transition

$$\hat{D}(t) \rightarrow \hat{\tilde{D}}(\tilde{t}) = \{\varepsilon_D \hat{D}[t(\tilde{t})]\}^* = \varepsilon_D \hat{D}^*(-\tilde{t}), \quad (5.3.27)$$

or more briefly, the transition $D(t) \rightarrow \varepsilon_D D^*(-\tilde{t})$ of the type (5.3.21) is valid for all possible times t . We note that the time-symmetry relation (5.3.26) imply an analogous relation for the equilibrium (canonical and microcanonical) density matrix

$$R(q, -p) = R(q, p), \quad (R(\hat{q}, \hat{p})^{(s)} = \hat{\rho}_{eq}). \quad (5.3.28)$$

This relation provides evidence for the time reversibility of the equilibrium state in the case of the reversible Hamiltonian.

Let us consider the set of operators $\hat{D}_1(t), \dots, \hat{D}_s(t)$ having the time signatures $\varepsilon_1, \dots, \varepsilon_s$ which show the time parity of these operators. We consider the equilibrium moment

$$\langle \hat{D}_1(t_1) \dots \hat{D}_s(t_s) \rangle_0 = \text{Tr} \{ \hat{D}_1(t_1) \dots \hat{D}_s(t_s) \hat{\rho}_0 \}. \quad (5.3.29)$$

By virtue of (5.3.27), the time-reversed expression

$$\begin{aligned} \text{Tr} \{ \hat{D}_1(\tilde{t}_1) \dots \hat{D}_s(\tilde{t}_s) \hat{\rho}_0 \} &= \varepsilon_1 \dots \varepsilon_s \text{Tr} \{ \hat{D}_1^*(-\tilde{t}_1) \dots \hat{D}_s^*(-\tilde{t}_s) \hat{\rho}_0^* \} \\ &= \varepsilon_1 \dots \varepsilon_s \langle \hat{D}_1(-\tilde{t}_1) \dots \hat{D}_s(-\tilde{t}_s) \rangle_0^*. \end{aligned} \quad (5.3.30)$$

corresponds to (5.3.29).

The moment (5.3.29) is invariant under time-reversal if in direct time it is the same function of the corresponding instants as in reverse time, i.e. if we have

$$\begin{aligned} \langle \hat{D}_1(t) \dots \hat{D}_s(t_s) \rangle_0 &= F(t_1, \dots, t_s), \\ \langle \hat{D}_1(\tilde{t}_1) \dots \hat{D}_s(\tilde{t}_s) \rangle_0 &= \varepsilon_1 \dots \varepsilon_s \langle \hat{D}_1(-\tilde{t}_1) \dots \hat{D}_s(-\tilde{t}_s) \rangle_s^* = F(\tilde{t}_1, \dots, \tilde{t}_s) \end{aligned} \quad (5.3.31)$$

where F is some function. From (5.3.31) it follows that the condition of moment invariance has the form

$$\varepsilon_1 \dots \varepsilon_s \langle \hat{D}_1(-t_1) \dots \hat{D}_s(-t_s) \rangle_0^* = \langle \hat{D}_1(t_1) \dots \hat{D}_s(t_s) \rangle_0. \quad (5.3.32)$$

The combined operation of (1) multiplication by a product of signatures $\varepsilon_1 \dots \varepsilon_s$, (2) change of signs of all the times t_i and (3) complex conjugation will be called the time conjugation operation. It will be denoted as follows:

$$\langle \hat{D}_1(t_1) \dots \hat{D}_s(t_s) \rangle_0^{tc} = \varepsilon_1 \dots \varepsilon_s \langle \hat{D}_1(-t_1) \dots \hat{D}_s(-t_s) \rangle_0^*. \quad (5.3.33)$$

This last formula generalizes formulas (5.1.23, 75), which define the operation of time conjugation in the nonquantum case, to the quantum case. We see that in the quantum case the operation of complex conjugation is added.

By virtue of (5.3.33) the condition (5.3.32) of time invariance of moments can be written as

$$\langle \hat{D}_1(t_1) \dots \hat{D}_s(t_s) \rangle_0^{t.c.} = \langle \hat{D}_1(t_1) \dots \hat{D}_s(t_s) \rangle_0 . \quad (5.3.34)$$

This condition was proved by Efremov [5.6]. The moment invariance follows from the Hamiltonian invariance (5.3.26).

We note that the correspondences (5.3.21, 25, 27) between the operators of direct time and reverse time are not the only possible ones. We can take

$$\hat{D}(\tilde{t}) = \hat{U} \varepsilon_D \hat{D}^*(-\tilde{t}) \hat{U}^{-1} \quad (5.3.35)$$

instead of (5.3.27). Here \hat{U} is an arbitrary unitary operator. Then (5.3.25) take the forms

$$\hat{U} \hat{\mathcal{H}}^* \hat{U}^{-1} = \hat{\mathcal{H}} . \quad (5.3.36)$$

However we can use simpler formulas (5.3.25, 27). It is easy to see that (5.3.34) follows from (5.3.31) in the case (5.3.35) as well.

Now we return to (5.3.26). Let the operators \hat{D}_j be represented as functions of \hat{q} , \hat{p} with symmetrization ordering

$$\hat{D}_j = f_j(\hat{q}, \hat{p})^{(s)} , \quad (5.3.37)$$

provided that functions f_j are real for Hermitian \hat{D}_j . Operators (5.3.37) have a definite parity if

$$f_j(q, -p) = \varepsilon_j f_j(q, p) . \quad (5.3.38)$$

The time-reversed operators are defined by the formulas analogous to (5.3.37)

$$\hat{D}_j = f_j(\hat{q}, \hat{p})^{(s)} . \quad (5.3.39)$$

Using (5.3.37–39), we can easily corroborate (5.3.21), since $\hat{q} = \hat{q}^*$, $\hat{p} = -\hat{p}^*$. Now we represent the Hamiltonian in the symmetrized form

$$\hat{\mathcal{H}} = H_1(\hat{q}, \hat{p})^{(s)} \quad (5.3.40)$$

with real H_1 . The time reversibility takes place when the time-reversed Hamiltonian is expressed in an analogous way in terms of \hat{q} , \hat{p} with the same function H_1 :

$$\hat{\mathcal{H}} = H_1(\hat{q}, \hat{p})^{(s)} . \quad (5.3.41)$$

Using equations $\hat{q} = \hat{q}^*$, $\hat{p} = -\hat{p}^*$, from (5.3.25, 41, 44) we obtain

$$H_1(q, -p) = H_1(q, p) .$$

Thus, (5.3.26) or (5.3.41) can be regarded as the condition of time reversibility. Obviously, (5.3.26) is analogous to (3.2.1). We see that $\hat{\mathcal{H}}$ is time-even.

When the external forces varying in time act on the system and the complete Hamiltonian is of the form (5.2.32), formula (5.3.33) for the moments corresponds to the unperturbed Hamiltonian $\hat{\mathcal{H}}_0$:

$$\langle \hat{D}_1^0(t_1) \dots \hat{D}_s^0(t_s) \rangle^{t.c.} = \langle \hat{D}_1^0(t_1) \dots \hat{D}_s^0(t_s) \rangle . \quad (5.3.42)$$

Here

$$\hat{D}_j^0(t) = \exp(i\hat{\mathcal{H}}_0 t/\hbar) \hat{D}_j \exp(-i\hat{\mathcal{H}}_0 t/\hbar).$$

In concluding this section we note that, using equations of the type (2.1.12, 15) generalized to the quantum case, one can derive from (5.3.42) analogous formulas for the correlators

$$\langle \hat{D}_1^0(t_1), \dots, \hat{D}_s^0(t_s) \rangle^{t.c.} = \langle \hat{D}_1^0(t_1), \dots, \hat{D}_s^0(t_s) \rangle. \quad (5.3.43)$$

5.3.3 Reciprocal Relations of Linear Theory

On setting in (5.3.43) $\hat{D}_1(t) = \hat{B}_{\alpha_1}(t)$ and $\hat{D}_2(t) = \hat{B}_{\alpha_2}(t)$ we obtain

$$\langle \hat{B}_1, \hat{B}_2 \rangle_{h \equiv 0}^{t.c.} = \langle \hat{B}_1, \hat{B}_2 \rangle_{h \equiv 0}.$$

Substituting (5.3.6) into the preceding equation and using (5.3.33), we arrive at

$$\begin{aligned} & -i\hbar \varepsilon_\alpha \varepsilon_\beta (\Gamma_2^-)^{t.c.} [G_{\alpha,\beta}(-t_1 + t_2) - G_{\beta,\alpha}(-t_2 + t_1)]^* \\ & = i\hbar \Gamma_2^- [G_{\alpha,\beta}(t_1 - t_2) - G_{\beta,\alpha}(t_2 - t_1)]. \end{aligned} \quad (5.3.44)$$

Taking into consideration (5.2.74, 79), it is easy to verify that the operators Γ^\pm are invariant under time conjugation: $\Gamma^\pm(p)^{t.c.} = \Gamma^\pm(p)$. One can therefore omit Γ_2^- in (5.3.44). As a consequence of the law of causality (5.2.6), we have $G_{\gamma,\delta}(t_{21}) = 0$ for $t_1 > t_2$. Therefore, from (5.3.44) we obtain

$$\varepsilon_\alpha \varepsilon_\beta G_{\beta,\alpha}(t_{12}) = G_{\alpha,\beta}(t_{12}) \quad (5.3.45)$$

(we have used the fact that $G_{\beta,\alpha}(t_{12})$ is real). The last equation can be written in the shorter form

$$G_{2,1}^{t.c.} = G_{1,2}. \quad (5.3.46)$$

Hence, in the spectral representation defined by (5.3.14b) we get

$$\varepsilon_\alpha \varepsilon_\beta G'_{\beta,\alpha}(\omega) = G'_{\alpha,\beta}(\omega). \quad (5.3.47)$$

The reciprocal relations (5.3.45, 47) are analogous to (5.1.15, 21). By virtue of (5.3.46), equations (5.3.6, 13) can be written as

$$\langle \hat{B}_1, \hat{B}_2 \rangle_0 = i\hbar \Gamma_2^- (G_{1,2} - G_{1,2}^{t.c.}), \quad (5.3.48a)$$

$$S_{\alpha\beta}(\omega) = \frac{i\hbar}{2} \coth\left(\frac{\hbar\omega}{2kT}\right) [G'_{\alpha,\beta}(\omega) - \varepsilon_\alpha \varepsilon_\beta G'^*_\alpha(\omega)]. \quad (5.3.48b)$$

In particular, for $\varepsilon_\alpha \varepsilon_\beta = 1$ we get

$$S_{\alpha\beta}(\omega) = -\hbar \coth\left(\frac{\hbar\omega}{2kT}\right) \text{Im}\{G'_{\alpha,\beta}(\omega)\}. \quad (5.3.49)$$

This form of linear FDT is frequently used.

5.3.4 Quadratic FDT

Let us express the equilibrium correlator $\langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle_0$ in terms of the quadratic admittance $G_{1,23}$ using (5.2.98). By virtue of the identity (5.2.103), which implies an equation of the type $\Gamma_{12}^+ = -\Gamma_3^-$ for $p_1 + p_2 + p_3 = 0$, (5.2.98) can be written as

$$\langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle_0 = -\Gamma_1^+(\Gamma_3^- V_{123} + \Gamma_2^+ V_{132}). \quad (5.3.50)$$

As is easy to verify directly, the mean of the repeated commutator

$$\begin{aligned} V_{123} &= \langle [[\hat{B}_1, \hat{B}_2], \hat{B}_3] \rangle_0 \\ &= \langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \rangle_0 - \langle \hat{B}_2 \hat{B}_1 \hat{B}_3 \rangle_0 - \langle \hat{B}_3 \hat{B}_1 \hat{B}_2 \rangle_0 + \langle \hat{B}_3 \hat{B}_2 \hat{B}_1 \rangle_0, \end{aligned} \quad (5.3.51)$$

has the symmetry properties

$$V_{123} = -V_{213}, \quad (5.3.52a)$$

$$V_{123} + V_{231} + V_{312} = 0. \quad (5.3.52b)$$

Using (5.3.52), we express the function V_{123} in terms of the partial functions a_{123} and b_{123} . The functions a_{klm}, b_{klm}, \dots which are nonzero only in the region $t_k > t_l > t_m$ or, in other words, satisfy equations of the type

$$a_{123}\eta_{123} = a_{123} \quad (5.3.53)$$

are called partial functions. Points where $t_k = t_l, t_l = t_m, t_k = t_m$, or $t_k = t_l = t_m$ are not considered. It is obvious that V_{123} can be expressed in terms of partial functions as follows

$$\begin{aligned} V_{123} &= V_{123}\eta_{123} + V_{123}\eta_{213} + V_{123}\eta_{231} + V_{123}\eta_{132} \\ &\quad + V_{123}\eta_{312} + V_{123}\eta_{321}. \end{aligned} \quad (5.3.54)$$

Conditions (5.3.52) decrease the number of independent partial functions. Using them, instead of (5.3.54) we can obtain

$$V_{123} = a_{123} - a_{213} + b_{231} - b_{132} - a_{312} - b_{312} + a_{321} + b_{321}, \quad (5.3.55)$$

where $a_{123} = V_{123}\eta_{123}$ and $b_{213} = V_{123}\eta_{213}$. It is easy to verify that the right-hand side of (5.3.55) satisfies the conditions (5.3.52). We see that there are two independent partial functions. A further decrease of the number of independent partial functions is provided by the time-symmetry condition. In fact, from the condition

$$\langle \hat{B}_k, \hat{B}_l, \hat{B}_m \rangle_0^{t.c.} = \langle \hat{B}_k, \hat{B}_l, \hat{B}_m \rangle_0 \quad (5.3.56)$$

[see (5.3.43)], which is a consequence of the time symmetry (5.3.26) of the Hamiltonian, we have by virtue of (5.3.51)

$$V_{123}^{t.c.} = V_{123}. \quad (5.3.57)$$

Substituting (5.3.55) into (5.3.57), we can express the function b in terms of a . Actually $a_{123}^{t.c.}$ is nonzero only in the region $t_3 > t_2 > t_1$. Hence, assuming that $t_3 > t_2 > t_1$ in the equation obtained by substitution of (5.3.55) into (5.3.57), we find $a_{123}^{t.c.} = a_{321} + b_{321}$, i.e.

$$b_{123} = a_{321}^{t.c.} - a_{123}. \quad (5.3.58)$$

Considering other regions, we get in addition

$$b_{231}^{t.c.} = -b_{132}. \quad (5.3.59)$$

The last equation may be also obtained from (5.3.58). Consequently, it is not an independent one and can be omitted.

Substituting (5.3.58) into (5.3.55), we obtain

$$V_{123} = a_{123} - a_{213} + a_{132} - a_{231} + t.c., \quad (5.3.60)$$

where t.c. denotes the sum of the time conjugates of the same terms.

We now use (5.2.58) for $m = 3$. Substituting (5.3.60), instead of $\langle [\hat{B}_1, \hat{B}_2], \hat{B}_3 \rangle_0$, into (5.2.58), we arrive at

$$G_{1,23} \eta_{123} = (i/\hbar)^2 a_{123}. \quad (5.3.61)$$

Hence, as a consequence of the symmetry $G_{1,23} = G_{1,32}$ [see (5.2.5)] we get

$$G_{1,23} = -\hbar^{-2}(a_{123} + a_{132}). \quad (5.3.62)$$

Because of (5.3.62), equation (5.3.60) can be written as

$$V_{123} = -\hbar^2(G_{1,23} - G_{2,13} + t.c.). \quad (5.3.63)$$

Thus, the function V_{123} in (5.3.50) has been expressed in terms of the admittance $G_{1,23}$. Therefore, the equilibrium correlator $\langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle_0 \equiv G_{1,23}$ can be expressed in terms of $G_{1,23}$. Substituting (5.3.63) into (5.3.50), we find

$$\begin{aligned} G_{123} = \hbar^2 & \Gamma_1^+ \{ \Gamma_3^- (G_{1,23} + G_{1,23}^{t.c.} - G_{2,13} - G_{2,13}^{t.c.}) \\ & + \Gamma_2^+ (G_{1,23} + G_{1,23}^{t.c.} - G_{3,12} - G_{3,12}^{t.c.}) \}. \end{aligned} \quad (5.3.64)$$

By using (5.2.104), formula (5.3.64) can be transformed to a more symmetrical form:

$$\begin{aligned} G_{123} \equiv \langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle_0 = & -\hbar^2 [\Gamma_2^- \Gamma_3^- (G_{1,23} + G_{1,23}^{t.c.}) \\ & + \Gamma_1^+ \Gamma_3^- (G_{2,13} + G_{2,13}^{t.c.}) \\ & + \Gamma_1^+ \Gamma_2^+ (G_{3,12} + G_{3,12}^{t.c.})]. \end{aligned} \quad (5.3.65)$$

The last equation is one of the formulations of the quadratic FDT. It was obtained in this form in 1970 [5.7]. Note that in the case of time-even parameters (when all $\varepsilon_\alpha = 1$), one can take $2 \operatorname{Re}\{G_{k,l,m}\}$ instead of $G_{k,l,m} + G_{k,l,m}^{t.c.}$ in the spectral representation since the change in the sign of the frequency caused by time conjugation leads to the complex conjugate admittance. As is noted in Sect. 5.2.4, the equilibrium moment is determined by a formula identical with (5.3.50) and, consequently, by the same formula (5.3.65).

5.3.5 Other Forms of Quadratic FDT

From (5.3.65) it is easy to find the symmetrized correlator

$$\begin{aligned} G_{123}^{\text{sym}} &= \frac{1}{4} \langle \langle [\hat{B}_1, \hat{B}_2]_+, \hat{B}_3 \rangle_+ \rangle_0 \\ &= \frac{1}{4} (G_{123} + G_{213} + G_{312} + G_{321}), \end{aligned} \quad (5.3.66)$$

which coincides with symmetrized moment $\frac{1}{4}\langle[[\hat{B}_1, \hat{B}_2]_+, \hat{B}_3]_+\rangle_0$ for $\langle\hat{B}_k\rangle_0 = 0$. It is convenient to begin with

$$G_{123} = -\hbar^2 \Gamma_3^- [\Gamma_2^- (G_{1,23} + G_{1,23}^{t.c.} - G_{3,12} - G_{3,12}^{t.c.}) + \Gamma_1^+ (G_{2,13} + G_{2,13}^{t.c.} - G_{3,12} - G_{3,12}^{t.c.})], \quad (5.3.67)$$

which has been obtained from (5.3.65) by using (5.2.104). In the time representation, the operators $\hat{B}_k = \hat{B}_{\alpha_k}(t_k)$ are Hermitian, and we therefore have in this representation

$$G_{123}^{\text{sym}} = \frac{1}{2} \operatorname{Re} \{G_{123} + G_{213}\}. \quad (5.3.68)$$

Using (5.3.10), we find from (5.3.67)

$$\begin{aligned} \frac{1}{2}(G_{123} + G_{213}) &= -\hbar^2 \Gamma_3^- [\Gamma_2 (G_{1,23} + G_{1,23}^{t.c.} - G_{3,12} - G_{3,12}^{t.c.}) \\ &\quad + \Gamma_1 (G_{2,13} + G_{2,13}^{t.c.} - G_{3,12} - G_{3,12}^{t.c.})]. \end{aligned} \quad (5.3.69)$$

Let us substitute formula (5.3.69) taken in the time representation into (5.3.68). Since the admittance $G_{k,lm}$ is real in the time representation and since, according to (5.2.74) and (5.3.10), operators Γ^- , Γ have the properties

$$[\Gamma^+(p)]^* = \Gamma^+(-p) = -\Gamma^-(p), \quad [\Gamma(p)]^* = \Gamma(-p) = -\Gamma(p) \quad (5.3.70)$$

in this representation, after the substitution into (5.3.68) we arrive at

$$\begin{aligned} \frac{1}{4}\langle\langle[[\hat{B}_1, \hat{B}_2]_+, \hat{B}_3]_+\rangle\rangle_0 &= -\hbar^2 \Gamma_3 P_{12} [\Gamma_2 (G_{1,23} + G_{1,23}^{t.c.} \\ &\quad - G_{3,12} - G_{3,12}^{t.c.})]. \end{aligned} \quad (5.3.71)$$

Here P_{12} denotes the sum over permutations of subscripts 1 and 2. Of course, the last formula is valid not only in the time representation.

The result (5.3.71) was obtained by Efremov in 1968 [5.8].

We now pass to the nonquantum limit $\hbar \rightarrow 0$ in (5.3.65) or in (5.3.67). Since $\hbar\Gamma^\pm(p) \rightarrow kT(ip)^{-1}$, $\hbar\Gamma(p) \rightarrow kT(ip)^{-1}$ for $\hbar \rightarrow 0$, as is seen from (5.2.74, 79), formula (5.3.65) or (5.3.67) goes over into

$$G_{123} \equiv \langle B_1, B_2, B_3 \rangle_0 = (kT)^2 P_{(123)} [p_2^{-1} p_3^{-1} (G_{1,23} + G_{1,23}^{t.c.})], \quad (5.3.72)$$

where $P_{(123)}$ denotes the summation over the cyclic permutations of subscripts 1, 2, 3. In particular, from (5.3.72) for time-even operators B_α in the spectral representation we have

$$\begin{aligned} \langle B_{\alpha_1}(\omega_1), B_{\alpha_2}(\omega_2), B_{\alpha_3}(\omega_3) \rangle_0 \\ = -2(kT)^2 P_{(123)} [\omega_2^{-1} \omega_3^{-1} \operatorname{Re} G'_{\alpha_1, \alpha_2, \alpha_3}(\omega_1, \omega_2)] \delta(\omega_1 + \omega_2 + \omega_3), \end{aligned} \quad (5.3.73)$$

where

$$B_\alpha(\omega) = (2\pi)^{-1/2} \int \exp(-i\omega t) B_\alpha(t) dt, \quad (5.3.74a)$$

$$G'_{\alpha, \beta\gamma}(\omega_1, \omega_2) = (2\pi)^{-1/2} \int \exp(-i\omega_1 t_{13} - i\omega_2 t_{23}) G_{\alpha, \beta\gamma}(t_1, t_2, t_3) dt_{13} dt_{23}. \quad (5.3.74b)$$

If in the time representation we differentiate both sides of (5.3.72) with respect to t_1, t_2, t_3 , we arrive at

$$\langle \dot{B}_1, \dot{B}_2, \dot{B}_3 \rangle_0 \equiv \langle J_1, J_2, J_3 \rangle_0 = (kT)^2 P_{(123)}(Y_{1,23} - Y_{1,23}^{t.c.}), \quad (5.3.75)$$

where according to (5.2.7) $Y_{1,23} = \partial/\partial t_1 G_{1,23} = p_1 G_{1,23}$. In (5.3.75) we have used that $(p_1 G_{1,23})^{t.c.} = p_1^{t.c.} G_{1,23}^{t.c.} = -p_1 G_{1,23}^{t.c.}$.

The correlator $\langle \dot{B}_1, \dot{B}_2, \dot{B}_3 \rangle_0$ is equal to the moment $\langle \dot{B}_1 \dot{B}_2 \dot{B}_3 \rangle_0$, since $\langle \dot{B}_l \rangle_0$ is always equal to zero owing to the stationarity of the equilibrium fluctuations.

Relation (5.3.75) is valid for all values of t_1, t_2, t_3 . If we take the region where the moments of time are ordered, say, where inequalities $t_1 > t_2 > t_3$ are valid, we can take into account a smaller number of terms in the expression for the correlator

$$\beta^2 \langle \dot{B}_\alpha(t_1), \dot{B}_\gamma(t_2), \dot{B}_\delta(t_3) \rangle_0 = Y_{\alpha,\gamma\delta}(t_1, t_2, t_3) - \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma Y_{\delta,\gamma\alpha}(-t_3, -t_2, -t_1). \quad (5.3.76)$$

As is easy to verify, the other terms give zero contribution in this region.

A physical system is called a mixing system if different correlators including $\langle B_1, B_2, B_3 \rangle_0$ and $\langle \dot{B}_1, \dot{B}_2, \dot{B}_3 \rangle_0$ tend to zero when the modulus of, at least, one time difference $t_1 - t_m$ corresponding to operators entering the correlator becomes infinitely large. For mixing system functions, $Y_{1,23}$ and $G_{1,23}$ must tend to zero sufficiently fast when the modulus of at least one difference $t_1 - t_m$ becomes infinitely large. In fact, from (5.3.75) or (5.3.76) it is seen that for the vanishing of the correlator $\langle \dot{B}_1, \dot{B}_2, \dot{B}_3 \rangle_0$ for $\max_{l,m} |t_l - t_m| \rightarrow \infty$ it is necessary that $Y_{1,23} \rightarrow 0$.

In order to find the correlator $\langle B_1, B_2, B_3 \rangle_0$ in the time representation, (5.3.75) should be integrated with respect to t_1, t_2, t_3 . In carrying out the integration we should make precise the integration constants or the arbitrary functions (because of the presence of several variables) in the given case. The uncertainty appearing here has the form of the sum

$$\varphi(t_{23}) + \varphi'(t_{12}) + \varphi''(t_{13}) + \text{const.} \quad (5.3.77)$$

which becomes zero when we let the operator $p_1 p_2 p_3$ act on it. Here $\varphi, \varphi', \varphi''$ are arbitrary functions. Specifying the sum (5.3.77), from (5.3.75), after integration, we can obtain both the correlator and the moment (they differ for $\langle B_l \rangle_0 \neq 0$). In formula (5.3.72) taken in the time representation we also have the integration that corresponds to operators $(p_2 p_3)^{-1}, (p_1 p_3)^{-1}, (p_1 p_2)^{-1}$. Owing to integration, an arbitrary additive expression (5.3.77) also appears.

In the case of mixing system, correlator $\langle B_1, B_2, B_3 \rangle_0$ tends to zero for $\max_{l,m} |t_l - t_m| \rightarrow 0$, but expression (5.3.77) does not tend to zero in the general case. This difference in behaviour should be used to find an expression for the correlator without arbitrary additive terms. Using the aforementioned property of $\langle B_1, B_2, B_3 \rangle_0$, from (5.3.76) we obtain

$$\begin{aligned} \beta^2 \langle B_\alpha(t_1), B_\gamma(t_2), B_\delta(t_3) \rangle_0 &= \int_{-\infty}^{t_2} \int_{-\infty}^{t_3} G_{\alpha,\gamma\delta}(t_1, t', t'') dt' dt'' \\ &\quad - \varepsilon_\alpha \varepsilon_\gamma \varepsilon_\delta \int_{\substack{t_3 - \varepsilon \\ \varepsilon \rightarrow 0}}^{t_2} dt' \int_{t_1}^{\infty} G_{\delta,\gamma\alpha}(-t_3, -t', -t'') dt'' \\ &\quad \text{for } t_1 \geq t_2 \geq t_3. \end{aligned} \quad (5.3.78)$$

In fact, if we perform the differentiation with respect to t_1, t_2, t_3 , we get (5.3.76), as can be easily verified. If in (5.3.78) we let $(t_1 - t_2)$ or $(t_2 - t_3)$ tend to infinity, we obtain zero in the limit (when the function $G_{1,23}$ tends to zero sufficiently fast when $\max(t_{12}, t_{23}) \rightarrow \infty$), as it must be in the case of a mixing system.

5.3.6 Three-Subscript Relation for Derivative of Correlator with Respect to External Force

The derivative of the correlator

$$\begin{aligned} G_{12,3} &= [\delta \langle \hat{B}_1, \hat{B}_2 \rangle / \delta h_3]_{h=0} \\ &= [\delta \langle \hat{B}_1 \hat{B}_2 \rangle / \delta h_3]_0 - [\delta \langle \hat{B}_1 \rangle / \delta h_3]_0 \langle \hat{B}_2 \rangle_0 \\ &\quad - \langle \hat{B}_1 \rangle_0 [\delta \langle \hat{B}_1 \rangle / \delta h_3]_0 \end{aligned} \quad (5.3.79)$$

at the equilibrium point will be called biadmittance. We suppose that $\langle \hat{B}_1 \rangle_0 = 0$. In this case we can use the formula $G_{12,3} = \delta \langle \hat{B}_1 \hat{B}_2 \rangle / \delta h_3$ at $h(t) \equiv 0$ instead of (5.3.79). One of the FDRs of the quadratic theory relates biadmittance $G_{12,3}$ to admittance $G_{1,23}$. Let us derive it. Evidently,

$$\frac{\delta(\hat{B}_1 \hat{B}_2)}{\delta h_3} = \frac{\delta \hat{B}_1}{\delta h_3} \hat{B}_2 + \hat{B}_1 \frac{\delta \hat{B}_2}{\delta h_3}. \quad (5.3.80)$$

On using (5.2.50) we obtain

$$\frac{\delta(\hat{B}_1 \hat{B}_2)}{\delta h_3} = \frac{i}{\hbar} \eta_{13} [\hat{B}_1, \hat{B}_3] B_2 + \frac{i}{\hbar} \eta_{23} \hat{B}_1 [\hat{B}_2, \hat{B}_3]. \quad (5.3.81)$$

Averaging (5.3.81) and setting $h(t) \equiv 0$, we arrive at

$$(i/\hbar) G_{12,3} = \eta_{13} \langle [\hat{B}_1, \hat{B}_3] \hat{B}_2 \rangle_0 + \eta_{23} \langle \hat{B}_1 [\hat{B}_2, \hat{B}_3] \rangle_0. \quad (5.3.82)$$

The right-hand side of (5.3.82) contains the equilibrium averages.

Using (5.2.77) with $\hat{D} = \hat{B}_1$ and $\hat{Q} = [\hat{B}_2, \hat{B}_3]$, we find

$$\langle \hat{B}_1 [\hat{B}_2, \hat{B}_3] \rangle_0 = \Gamma_1^+ \langle [\hat{B}_1, [\hat{B}_2, \hat{B}_3]] \rangle_0 = -\Gamma_1^+ V_{231} \quad (5.3.83)$$

and analogously

$$\langle [\hat{B}_1, \hat{B}_3] \hat{B}_2 \rangle_0 = \Gamma_1^+ \langle [[\hat{B}_1, \hat{B}_3], \hat{B}_2] \rangle_0 = -\Gamma_2^- V_{132}. \quad (5.3.84)$$

By virtue of (5.3.83, 84), equation (5.3.82) can be written in the form

$$i\hbar G_{12,3} = \eta_{13} (\Gamma_2^- V_{132}) + \eta_{23} (\Gamma_1^+ V_{231}). \quad (5.3.85)$$

Since in the time representation Γ_2^- contains $p_2 = \partial/\partial t_2$ and $\eta_{13} = \eta(t_1 - t_3)$ is independent of t_2 , function η_{13} commutes with Γ_2^- and η_{23} commutes with Γ_1^+ . Therefore, (5.3.85) can be written as

$$i\hbar G_{12,3} = \Gamma_2^- (\eta_{13} V_{132}) + \Gamma_1^+ (\eta_{23} V_{231}). \quad (5.3.86)$$

Using (5.3.60, 62), we easily obtain

$$\eta_{12} V_{123} = a_{123} + a_{132} - a_{213}^{t.c.} - a_{231}^{t.c.} = -\hbar^2 (G_{1,23} - G_{2,13}^{t.c.}). \quad (5.3.87)$$

Therefore, from (5.3.86) we find

$$-(i/\hbar)G_{12,3} = \Gamma_2^-(G_{1,32} - G_{3,12}^{t.c.}) + \Gamma_1^+(G_{2,31} - G_{3,21}^{t.c.}) \quad (5.3.88)$$

or

$$G_{12,3} = i\hbar[\Gamma_2^-G_{1,23} + \Gamma_1^+G_{2,13} - (\Gamma_2^- + \Gamma_1^+)G_{3,12}^{t.c.}] \quad (5.3.89)$$

This is the FDR sought.

If in (5.3.89) we interchange the subscripts 1 and 2 and then add the result to (5.3.89), we obtain the symmetrized biadmittance

$$\begin{aligned} G_{12,3}^{\text{sym}} &= \frac{1}{2} \left[\frac{\delta \langle [\hat{B}_1, \hat{B}_2]_+ \rangle}{\delta h_3} \right]_{h=0} = i\hbar[\Gamma_2 G_{1,23} + \Gamma_1 G_{2,13} \\ &\quad - (\Gamma_1 + \Gamma_2)G_{3,12}^{t.c.}] \end{aligned} \quad (5.3.90)$$

In the nonquantum limit $\hbar \rightarrow 0$, we get from (5.3.89) or (5.3.90)

$$\beta G_{12,3} = p_2^{-1}G_{1,23} + p_1^{-1}G_{2,13} + p_3 p_1^{-1} p_2^{-1} G_{3,21}^{t.c.} \quad (5.3.91)$$

This is one of the two nonquantum quadratic FDRs.

5.3.7 Linear and Quadratic FDRs with Modified Admittances

The function $Y_{1,23} = p_1 G_{1,23}$ is the modified quadratic admittance. Analogously, the linear modified admittance is defined by the equation $Y_{1,2} = p_1 G_{1,2}$. Using $Y_{1,2}$, after differentiation of both sides of (5.3.6) with respect to t_1 and t_2 we obtain

$$Y_{12} = kT\Theta_2^-(Y_{1,2} + Y_{2,1}) \quad (5.3.92)$$

Here we have designated $Y_{12} = \langle \dot{\hat{B}}_1, \dot{\hat{B}}_2 \rangle_0 = \langle \hat{J}_1, \hat{J}_2 \rangle_0$, and also

$$\Theta^\pm(p) = i\beta\hbar p\Gamma^\pm(p) \quad (5.3.93)$$

Differentiating (5.3.46) with respect to t_1 and using that $p_1 = -p_2$, we obtain the reciprocal relation for the modified admittance

$$Y_{1,2} = Y_{2,1}^{t.c.} \quad (5.3.94a)$$

or

$$Y_{\alpha,\beta}(t_{12}) = \varepsilon_\alpha \varepsilon_\beta Y_{\beta,\alpha}(t_{12}) \quad (5.3.94b)$$

Differentiating (5.3.65) with respect to t_1, t_2, t_3 , we can find a quantum quadratic FDR for the modified admittance:

$$\begin{aligned} Y_{123} &= (kT)^2 [\Theta_2^- \Theta_3^-(Y_{1,23} - Y_{1,23}^{t.c.}) + \Theta_1^+ \Theta_3^-(Y_{2,13} - Y_{2,13}^{t.c.}) \\ &\quad + \Theta_1^+ \Theta_2^+(Y_{3,12} - Y_{3,12}^{t.c.})], \end{aligned} \quad (5.3.95)$$

where

$$Y_{123} = \langle \hat{J}_1, \hat{J}_2, \hat{J}_3 \rangle_0 \quad (5.3.96)$$

Finally, differentiating (5.3.89) with respect to t_1 and t_2 and denoting $[\delta \langle \hat{J}_1, \hat{J}_2 \rangle / \delta h_3]_{h=0} = Y_{12,3}$, we arrive at

$$Y_{12,3} = kT[\Theta_2^- Y_{1,23} + \Theta_1^+ Y_{2,13} + (p_1 \Theta_2^- + p_2 \Theta_1^+) p_3^{-1} Y_{3,21}^{t.c.}] \quad (5.3.97)$$

From (5.3.95, 97) we readily obtain the symmetrized functions

$$\begin{aligned} \frac{1}{4}\langle\langle[\hat{J}_1, \hat{J}_2]_+, \hat{J}_3]_+\rangle\rangle_0 &= (kT)^2 [P_{12}\Theta_2\Theta_3(Y_{1,23} - Y_{1,23}^{t.c.}) \\ &\quad + \frac{1}{2}(\Theta_1^+ \Theta_2^+ + \Theta_1^- \Theta_2^-)(Y_{3,12} - Y_{3,12}^{t.c.})] , \end{aligned} \quad (5.3.98a)$$

$$\frac{1}{2}(\delta\langle\langle[\hat{J}_1, \hat{J}_2]_+\rangle\rangle/\delta h_3)_0 = kT[P_{12}\Theta_2 Y_{1,23} + (p_1\Theta_2 + p_2\Theta_1)p_3^{-1} Y_{3,21}^{t.c.}] , \quad (5.3.98b)$$

where $\Theta_l = (\Theta_l^+ + \Theta_l^-)/2$.

Operators Θ^\pm, Θ [see (5.3.93)] are defined such that they are equal to unity in the nonquantum limit $\hbar \rightarrow 0$. In this case (5.3.95) transforms to (5.3.75), and (5.3.97) transforms to the simple formula

$$\beta Y_{12,3} = Y_{1,23} + Y_{2,13} - Y_{3,12}^{t.c.} . \quad (5.3.99)$$

This formula is simpler than (5.3.91); however, (5.3.89) is somewhat simpler than (5.3.97). Therefore, we cannot say whether FDRs have simpler forms in terms of admittance G_{\dots} , or admittance Y_{\dots} .

5.3.8 Non-Markov FDRs of the Second Kind in the Case Where Energy Is One of the Parameters B_α

If many-time correlators of energy $\mathcal{H}_0(z)$ as well as correlators of the other parameters $B_\alpha(z)$, $\alpha = 1, \dots, r$ are of interest, we should somewhat modify the initial formula (5.2.1). Namely, introducing an external force $h_0(t)$ conjugate to $\mathcal{H}_0(z)$, we now write

$$\begin{aligned} \mathcal{H}(z, h(t)) &= \mathcal{H}_0(z) - \mathcal{H}_0(z)h_0(t) - \sum_{\alpha=1}^r B_\alpha(z)h_\alpha(t) \\ &= \mathcal{H}_0(z) - \sum_{\alpha=0}^r B_\alpha(z)h_\alpha(t) . \end{aligned} \quad (5.3.100)$$

In this case the FDRs derived in this section can be applied for finding many-time correlators of the various internal parameters including the energy $\mathcal{H}_0(z)$. To this end, we must only set $\alpha_1 = 0, 1, \dots, r$ in these correlators.

In the case when the unperturbed Hamiltonian corresponding to the values $h_0 = 0, h_1 = 0, \dots, h_r = 0$ is represented in the form

$$\mathcal{H}(z) = \mathcal{H}_0(z) - \sum_{\alpha=1}^r B_\alpha(z)a_\alpha^0 \quad (5.3.101)$$

[see (2.2.25)], instead of (5.3.100) we can take

$$\mathcal{H}(z, h(t)) = \mathcal{H}_0(z) - \mathcal{H}_0(z)h_0(t) - \sum_{\alpha=1}^r B_\alpha(z)(a_\alpha^0 + h_\alpha(t)) . \quad (5.3.102)$$

Let us consider a simple illustrative example.

Example. Suppose we have a system which is described by the unperturbed Hamiltonian \mathcal{H}_0 and which is in the thermal contact with a thermostat. When

external forces are absent, the contact is described by the relaxation equation

$$\dot{U}_0 = -\gamma(U_0 - U_0^0), \quad (5.3.103)$$

where $U_0 = \langle \mathcal{H}_0 \rangle$. We would like to find the equilibrium two-time correlator $\langle \mathcal{H}_0(t_1), \mathcal{H}_0(t_2) \rangle$.

To solve the problem, we write down, introducing the external “force” $h_0(t)$, the perturbed Hamiltonian (5.3.100), namely, the Hamiltonian

$$\mathcal{H}(z, h_0(t)) = \mathcal{H}_0(z)[1 - h_0(t)]. \quad (5.3.104)$$

If the admittance $G_{0,0}(t_1, t_2)$, determined by the ordinary formula,

$$\langle \mathcal{H}(t_1) \rangle = U_0^0 + \int G_{0,0}(t_1, t_2) h_0(t_2) dt_2 \quad (5.3.105)$$

[see (5.2.2)] is found, we only need to use a linear FDR for finding the correlator $\langle \mathcal{H}_0(t_1), \mathcal{H}_0(t_2) \rangle$. We now calculate this admittance.

At first we suppose that there is no heat exchange and find the time derivative $d\mathcal{H}/dt$. Using the Hamilton equations, we readily get

$$d\mathcal{H}(z, h(t))/dt = \partial\mathcal{H}(z, h(t))/\partial t = -\mathcal{H}_0(z)\dot{h}_0(t) \quad (5.3.106)$$

[(5.3.104) has been used]. Averaging (5.3.106) gives

$$d\langle \mathcal{H} \rangle/dt = -U_0^0\dot{h}_0(t). \quad (5.3.107)$$

Taking into consideration the presence of thermal contact, we can combine (5.3.107) with the relaxation equation (5.3.103); this yields

$$\dot{U}_0 = -\gamma(U_0 - U_0^0) - U_0^0\dot{h}_0(t). \quad (5.3.108)$$

Now, it is easy to obtain the unknown admittance from (5.3.108). In the spectral representation we have

$$G_{0,0}(\omega_1, \omega_2) = -i\omega_1(i\omega_1 + \gamma)^{-1}U_0^0\delta(\omega_1 + \omega_2). \quad (5.3.109)$$

We can apply the nonquantum linear FDR (5.3.11, 13) and obtain

$$\langle \mathcal{H}_0(\omega_1), \mathcal{H}_0(\omega_2) \rangle = 2kT\gamma U_0^0(\omega_1^2 + \gamma^2)^{-1}\delta(\omega_1 + \omega_2), \quad (5.3.110a)$$

$$S_{U_0}(\omega) = 2kT\gamma U_0^0(\omega^2 + \gamma^2)^{-1}. \quad (5.3.110b)$$

In the time representation, the correlator

$$\langle \mathcal{H}_0(t_1), \mathcal{H}_0(t_2) \rangle = kT U_0^0 \exp(-\gamma|t_{12}|) \quad (5.3.111)$$

corresponds to the spectral density (5.3.110b). The example that we have considered above is purely illustrative since this result can be easily obtained by using the linear Markov FDR and applying the method given in Sect. 4.4. The method of this section however has the advantage of paving the way for a well-justified quantum generalization. Besides, the method is useful for solving more complicated problems, e.g. nonlinear problems and problems with delay.

5.3.9 Modified Variant of FDRs of the Second Kind

The non-Markov FDRs can be reduced to the form that is analogous to a modified variant of the Markov theory (see Sects. 3.1.5, 3.2.5, 4.1.3). In the modified variant, instead of nonconstant thermodynamic forces $h_i(t)$ we consider forces $\bar{h}_i(t) = h_i(t)/T$, which are introduced by

$$T^{-1} \mathcal{H}(z, \bar{h}(t)) = T^{-1} \mathcal{H}_0(z) - \sum_{i=0}^r B_i(z) \bar{h}_i(t) \quad (5.3.112)$$

or

$$T^{-1} \mathcal{H}(z, \bar{h}(t)) = - \sum_{i=0}^r B_i(z) [\alpha_i^0 + \bar{h}_i(t)] . \quad (5.3.113)$$

Formulas (5.3.112, 113) replace (5.3.100, 102). If the forces \bar{h}_i do not change in time, then they coincide with thermodynamic forces which appear in the modified variant of the Markov nonequilibrium thermodynamics.

Naturally, in the modified variant, admittance should be introduced by

$$A_1 = A_1^0 + \bar{G}_{1,2} \bar{h}_2 + \frac{1}{2} \bar{G}_{1,23} \bar{h}_2 \bar{h}_3 + \frac{1}{6} \bar{G}_{1,234} \bar{h}_2 \bar{h}_3 \bar{h}_4 + \dots \quad (5.3.114)$$

instead of (5.2.4). It is easy to see that equations

$$\begin{aligned} \bar{G}_{1,2\dots m} &= T^{m-1} G_{1,2\dots m} \\ \bar{Y}_{1\dots l,(l+1)\dots m} &= T^{m-1} Y_{1\dots l,(l+1)\dots m} \end{aligned} \quad (5.3.115)$$

are valid. When we pass to the modified variant, FDRs of the second kind change somewhat. For example, instead of (5.3.92, 95) we get

$$Y_{12} = \bar{Y}_{12} = k \Theta_2^- (\bar{Y}_{1,2} + \bar{Y}_{2,1}) , \quad (5.3.116a)$$

$$\begin{aligned} Y_{123} = \bar{Y}_{123} &= k^2 [\Theta_2^- \Theta_3^- (\bar{Y}_{1,23} - \bar{Y}_{1,23}^{t.c.}) \\ &\quad + \Theta_1^+ \Theta_3^- (\bar{Y}_{2,13} - \bar{Y}_{2,13}^{t.c.}) + \Theta_1^+ \Theta_2^+ (\bar{Y}_{3,12} - \bar{Y}_{3,12}^{t.c.})] . \end{aligned} \quad (5.3.116b)$$

We see that the difference between the new formulas and the previous ones is that k is used instead of kT . It will be recalled that the difference between FDRs of the Markov modified variant and FDRs of the Markov main variant is the same as in the non-Markov case.

5.4 Cubic FDRs of the Second Kind

5.4.1 Formulas Pertaining to Four-Subscript Correlators and Commutators

Cubic FDRs establish universal relations between the following four-subscript functions:

1. admittance $G_{1,234}$,

2. biadmittance

$$G_{12,34} = \left[\frac{\delta^2 \langle \hat{B}_1, \hat{B}_2 \rangle}{\delta h_3 \delta h_4} \right]_{h=0}, \quad (5.4.1)$$

3. triadmittance

$$G_{123,4} = [\delta \langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle / \delta h_4]_{h=0}, \quad (5.4.2)$$

4. equilibrium correlator

$$G_{1234} = \langle \hat{B}_1, \hat{B}_2, \hat{B}_3, \hat{B}_4 \rangle_0. \quad (5.4.3)$$

Formula (5.2.102) will be now used. Using (5.2.103) and the definition (5.4.3) we can write (5.2.102) as

$$\begin{aligned} G_{1234} = & \Gamma_1^+ [\Gamma_{34}^- (\Gamma_4^- V_{1234} + \Gamma_3^+ V_{1243}) + \Gamma_{24}^+ \Gamma_4^- V_{1324} + \Gamma_{42}^- \Gamma_2^+ V_{1342} \\ & + \Gamma_{23}^+ (\Gamma_3^- V_{1423} + \Gamma_2^+ V_{1432})]. \end{aligned} \quad (5.4.4)$$

Let us consider the commutation function $V_{1234} = \langle [[[\hat{B}_1, \hat{B}_2], \hat{B}_3], \hat{B}_4] \rangle_0$. It satisfies equations of the form

$$V_{1234} + V_{2134} = 0, \quad (5.4.5a)$$

$$V_{1234} + V_{2314} + V_{3124} = 0, \quad (5.4.5b)$$

which are analogous to (5.3.52). Equation (5.4.5a) is valid because V_{1234} contains the commutator $[\hat{B}_1, \hat{B}_2]$ and (5.4.5b) is valid because the function V_{1234} contains the double commutator $[[\hat{B}_1, \hat{B}_2], \hat{B}_3]$. Writing this commutator in detail, we have

$$V_{1234} = G_{1234} - G_{2134} - G_{3124} + G_{3214} - G_{4123} + G_{4213} + G_{4312} - G_{4321}. \quad (5.4.6)$$

Using this equation, we easily verify that there is another symmetry relation

$$V_{1234} + V_{2143} + V_{3412} + V_{4321} = 0. \quad (5.4.7)$$

Finally, one more relation follows from the time reversibility condition. In fact, if condition (5.3.26) is fulfilled, then by virtue of (5.3.34), correlator (5.4.3) is invariant under time conjugation: $G_{1234}^{t.c.} = G_{1234}$. Using (5.4.6), we hence obtain

$$V_{1234}^{t.c.} = V_{1234}. \quad (5.4.8)$$

Let us use (5.4.5, 8) for writing the commutator V_{1234} in the form of a sum of partial functions. We take the following general variant of the expansion:

$$V_{1234} = V_{1234}^{(1)} + V_{1234}^{(2)}, \quad (5.4.9)$$

where

$$\begin{aligned} V_{1234}^{(1)} = & (a_{1234} - a_{2134} - a_{2314} + a_{1324}) \\ & + (a_{1243} - a_{2143} - a_{2341} + a_{1342}) \\ & + (a_{1423} - a_{2413} - a_{2431} + a_{1432}) + t.c. \end{aligned} \quad (5.4.10)$$

and

$$\begin{aligned} V_{1234}^{(2)} = & b_{2314} - b_{1324} - b_{3124} + b_{3214} + c_{1243} - c_{2143} \\ & + d_{2341} - d_{1342} - (c+d)_{3142} + (c+d)_{3241} + \text{t.c.} . \end{aligned} \quad (5.4.11)$$

The addition of the time conjugates, which are denoted by “t.c.”, ensures the validity of (5.4.8). Here a_{klmn} , b_{klmn} , c_{klmn} , d_{klmn} are the partial functions which are nonzero only in the region $t_k > t_l > t_m > t_n$. It is easy to verify that $V_{1234}^{(1)}$ and $V_{1234}^{(2)}$ separately satisfy (5.4.5) [each sum in parentheses in (5.4.10) satisfies (5.4.5)]. We see that V_{1234} is determined by four independent partial functions. Some relationships between them are given by equation (5.4.7), which has not been used as yet. The substitution of (5.4.9, 10, 11) into (5.4.7) leads to equations for the partial functions

$$\begin{aligned} c_{1234} + \tilde{c}_{1234} &= 0 , \\ b_{1234} + \tilde{b}_{1234} + d_{1234} + \tilde{d}_{1234} &= 0 , \end{aligned} \quad (5.4.12)$$

where we have denoted $\tilde{c}_{1234} = c_{4321}^{\text{t.c.}}$ and so on. Both functions \tilde{c}_{1234} and c_{1234} are nonzero in the same region.

Unlike (5.4.10), function (5.4.11) is equal to zero in the region $t_1 > t_2 > t_3 > t_4$. Therefore, if we substitute (5.4.9) into equation (5.2.28) for $m = 4$, we get

$$g_{1,234} = (\hbar/i)^{m-1} a_{1234} \quad (5.4.13)$$

since

$$V_{1234} \eta_{1234} = a_{1234} . \quad (5.4.14)$$

Consequently, function (5.4.10) can be found if the admittance $G_{1,234}$ is known. The function (5.4.10) is therefore said to be dissipationally determinable. Equations (5.4.12) are insufficient for determining the functions b , c , d (and, consequently, for determining $V_{1234}^{(2)}$) if the partial function (5.4.14) is known. The function (5.4.11) is therefore described as dissipationally undeterminable. For the complete determination of $V_{1234}^{(2)}$ we need to prescribe, say, the partial function b and the two “halves” ($c - \tilde{c}$) and ($d - \tilde{d}$). Thus, in the cubic theory (and also in the case of higher nonlinearities) one is unable to express correlator (5.4.3) and, consequently, the other functions (5.4.1, 2) in terms of the admittance $G_{1,234}$ completely. The possibility of expressing all functions with a fixed number of subscripts in terms of admittance is “the privilege” of the linear and quadratic theories. Recall that the notion of a dissipationally undeterminable part exists in the Markov theory as well (Sect. 4.1). In spite of the absence of this “privilege”, we have in the cubic theory relations connecting admittance and functions (5.4.1–3). They will be derived later.

By virtue of (5.2.60) and (5.4.14) we have $(\hbar/i)^3 G_{1234} = P_{234} a_{1234}$. Taking this equation and (5.4.13) into account, we easily verify that (5.4.10) can be written as

$$V_{1234}^{(1)} = (\hbar/i)^3 [G_{1,234} - G_{2,134} - \text{t.c.}] . \quad (5.4.15)$$

Equation (5.4.15) resembles formula (5.3.63) of the quadratic theory.

5.4.2 Relation for the Dissipationally Determinable Part of the Correlator

Substitution of (5.4.9) into (5.4.4) yields

$$G_{1234} = G_{1234}^{(1)} + G_{1234}^{(2)}, \quad (5.4.16)$$

where

$$\begin{aligned} G_{1234}^{(j)} &= \Gamma_1^+ [\Gamma_{34}^- (\Gamma_4^- V_{1234}^{(j)} + \Gamma_3^+ V_{1243}^{(j)}) \\ &\quad + \Gamma_{24}^+ \Gamma_4^- V_{1324}^{(j)} + \Gamma_{24}^- \Gamma_2^+ V_{1342}^{(j)} \\ &\quad + \Gamma_{23}^+ (\Gamma_3^- V_{1423}^{(j)} + \Gamma_2^+ V_{1432}^{(j)})], \quad j = 1, 2. \end{aligned} \quad (5.4.17)$$

We substitute (5.4.15) into equation (5.4.17) for $j = 1$ and collect like terms. Using admittance symmetry of the type (5.2.5), we find

$$\begin{aligned} G_{1234}^{(1)} &= -(\hbar/i)^3 \Gamma_1^+ [\Gamma_{34}^- (\Gamma_4^- + \Gamma_3^+) (G_{2,134} - G_{1,234}) \\ &\quad + (\Gamma_{24}^+ \Gamma_4^- + \Gamma_{24}^- \Gamma_2^+) (G_{3,124} - G_{1,234}) + \Gamma_{23}^+ (\Gamma_3^- + \Gamma_2^+) \\ &\quad \times (G_{4,123} - G_{1,234}) - \text{t.c.}] . \end{aligned} \quad (5.4.18)$$

On employing identities (5.2.107) we obtain

$$\begin{aligned} G_{1234}^{(1)} &= -i\hbar^3 \Gamma_1^+ [\Gamma_3^- \Gamma_4^- (G_{2,134} - G_{1,234}) + \Gamma_2^+ \Gamma_4^- (G_{3,124} - G_{1,234}) \\ &\quad + \Gamma_2^+ \Gamma_3^+ (G_{4,123} - G_{1,234}) - \text{t.c.}] . \end{aligned} \quad (5.4.19)$$

Finally, using (5.2.105), we arrive at

$$\begin{aligned} G_{1234}^{(1)} &= -i\hbar^3 [\Gamma_2^- \Gamma_3^- \Gamma_4^- (G_{1,234} - G_{1,234}^{\text{t.c.}}) + \Gamma_1^+ \Gamma_3^- \Gamma_4^- (G_{2,134} - G_{2,134}^{\text{t.c.}}) \\ &\quad + \Gamma_1^+ \Gamma_2^+ \Gamma_4^- (G_{3,124} - G_{3,124}^{\text{t.c.}}) + \Gamma_1^+ \Gamma_2^+ \Gamma_3^+ (G_{4,123} - G_{4,123}^{\text{t.c.}})] . \end{aligned} \quad (5.4.20)$$

We see that (5.4.20) has the same structure as (5.3.65). Let us now consider the symmetrized expression

$$\begin{aligned} G_{1234}^{(1)\text{sym}} &= \frac{1}{8} (G_{1234}^{(1)} + G_{2134}^{(1)} + G_{3124}^{(1)} + G_{3214}^{(1)} + G_{4123}^{(1)} \\ &\quad + G_{4213}^{(1)} + G_{4312}^{(1)} + G_{4321}^{(1)}) \\ &\equiv \frac{1}{8} \langle \langle [[[\hat{B}_1, \hat{B}_2]_+, \hat{B}_3]_+, \hat{B}_4]_+ \rangle \rangle , \end{aligned} \quad (5.4.21)$$

which is the correlator analogue of the symmetrized moment $\frac{1}{8} \langle \langle [[[\hat{B}_1, \hat{B}_2]_+, \hat{B}_3]_+, \hat{B}_4]_+ \rangle \rangle^{(1)}$. For expression (5.4.21), formula (5.4.19) implies

$$G_{1234}^{(1)\text{sym}} = -i\hbar^3 \Gamma_4 [\Gamma_3 P_{12} \Gamma_1 \tilde{G}_{2,134} + (\Gamma_1 \Gamma_2 + \frac{1}{4}) \tilde{G}_{3,124}], \quad (5.4.22)$$

where

$$\tilde{G}_{2,134} = G_{2,134} - G_{2,134}^{\text{t.c.}} - G_{4,123} + G_{4,123}^{\text{t.c.}} . \quad (5.4.23)$$

Formula (5.4.22) is analogous to formula (5.3.71) of the quadratic theory. From (5.4.20) or (5.4.22) we can easily obtain the dissipationally determinable part of the correlator that is completely symmetrized in all the subscripts. This expression is more complex, and we shall not give it here.

5.4.3 Dissipationally Determinable Part of the Triadmittance

Let us first find how the triadmittance (5.4.2) can be expressed in terms of the commutator V_{1234} . We have

$$\frac{\delta(\hat{B}_1 \hat{B}_2 \hat{B}_3)}{\delta h_4} = \frac{\delta \hat{B}_1}{\delta h_4} \hat{B}_2 \hat{B}_3 + \hat{B}_1 \frac{\delta \hat{B}_2}{\delta h_4} \hat{B}_3 + \hat{B}_1 \hat{B}_2 \frac{\delta \hat{B}_3}{\delta h_4}. \quad (5.4.24)$$

In view of (5.2.50), we obtain

$$\begin{aligned} \delta(\hat{B}_1 \hat{B}_2 \hat{B}_3)/\delta h_4 &= (i/\hbar)(\eta_{14}[\hat{B}_1, \hat{B}_4]\hat{B}_2 \hat{B}_3 + \eta_{24}\hat{B}_1[\hat{B}_2, \hat{B}_4]\hat{B}_3 \\ &\quad + \eta_{34}\hat{B}_1\hat{B}_2[\hat{B}_3, \hat{B}_4]). \end{aligned} \quad (5.4.25)$$

The triadmittance (5.4.2) can therefore be written as

$$\begin{aligned} (\hbar/i)[\delta \langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \rangle / \delta h_4]_{h=0} &= \eta_{14} \langle [\hat{B}_1, \hat{B}_4] \hat{B}_2 \hat{B}_3 \rangle_0 \\ &\quad + \eta_{24} \langle \hat{B}_1 [\hat{B}_2, \hat{B}_4] \hat{B}_3 \rangle_0 \\ &\quad + \eta_{34} \langle \hat{B}_1 \hat{B}_2 [\hat{B}_3, \hat{B}_4] \rangle_0. \end{aligned} \quad (5.4.26)$$

Using formulas (5.2.86, 88, 89) with $\hat{D} = [\hat{B}_k, \hat{B}_4]$, we find from (5.4.26)

$$\begin{aligned} (\hbar/i)G_{123,4} &= \eta_{14}\Gamma_{23}^-\Gamma_3^-V_{1423} + \eta_{14}\Gamma_{23}^+\Gamma_2^+V_{1432} \\ &\quad + \eta_{24}\Gamma_{13}^+\Gamma_3^-V_{2413} + \eta_{24}\Gamma_{13}^-\Gamma_1^+V_{2431} \\ &\quad + \eta_{34}\Gamma_{12}^+\Gamma_2^-V_{3412} + \eta_{34}\Gamma_{12}^+\Gamma_1^+V_{3421}. \end{aligned} \quad (5.4.27)$$

Here (5.2.103) has been used. In (5.4.27) we have written the biadmittance (5.4.2) instead of $[\delta \langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \rangle / \delta h_4]_0$ since the same formula is valid for both functions (because of the presence of operators Γ^\pm). In the first term on the right-hand side of (5.4.27) one can interchange η_{14} and $\Gamma_{23}^-\Gamma_3^-$. The justification for this rearrangement is provided by the fact that t_1 and t_4 appear in η_{14} and that the operators $p_2 = \partial/\partial t_2$ and $p_3 = \partial/\partial t_3$ appear in $\Gamma_{23}^-, \Gamma_3^-$. Analogous rearrangements are made in the other terms as well. Then, substituting (5.4.9), we obtain from (5.4.27)

$$G_{123,4} = G_{123,4}^{(1)} + G_{123,4}^{(2)}, \quad (5.4.28)$$

where

$$\begin{aligned} (\hbar/i)G_{123,4}^{(j)} &= \Gamma_{23}^-(\Gamma_3^-(\eta_{14}V_{1423}^{(j)}) + \Gamma_2^+(\eta_{14}V_{1432}^{(j)})) \\ &\quad + \Gamma_{13}^+\Gamma_3^-(\eta_{24}V_{2413}^{(j)}) + \Gamma_{13}^-\Gamma_1^+(\eta_{24}V_{2431}^{(j)}) \\ &\quad + \Gamma_{12}^+(\Gamma_2^-(\eta_{34}V_{3412}^{(j)}) + \Gamma_1^+(\eta_{34}V_{3421}^{(j)})) \quad (j = 1, 2). \end{aligned} \quad (5.4.29)$$

From (5.4.15) we find

$$\eta_{12}V_{1234}^{(1)} = (\hbar/i)^3(G_{1,234} + G_{2,134}^{t.c.}). \quad (5.4.30)$$

Substituting this into equation (5.4.29) for $j = 1$, we obtain the dissipationally determinable part of the triadmittance

$$\begin{aligned} (\hbar/i)^2 G_{123,4}^{(1)} &= \Gamma_{23}^-(\Gamma_3^- + \Gamma_2^+)(G_{1,234} + G_{4,123}^{t.c.}) + (\Gamma_{13}^+\Gamma_3^- + \Gamma_{13}^-\Gamma_1^+) \\ &\quad \times (G_{2,134} + G_{4,123}^{t.c.}) + \Gamma_{12}^+(\Gamma_2^- + \Gamma_1^+)(G_{3,124} + G_{4,123}^{t.c.}) \end{aligned} \quad (5.4.31)$$

or, if we use (5.2.107),

$$\begin{aligned} G_{123,4}^{(1)} = & -\hbar^2 [\Gamma_2^- \Gamma_3^- G_{1,234} + \Gamma_1^+ \Gamma_3^- G_{2,134} + \Gamma_1^+ \Gamma_2^+ G_{3,124} \\ & + (\Gamma_2^- \Gamma_3^- + \Gamma_1^+ \Gamma_3^- + \Gamma_1^+ \Gamma_2^+) G_{4,123}^{t.c.}] . \end{aligned} \quad (5.4.32)$$

Hence, in particular, it is easy to obtain an expression for the symmetrized triadmittance

$$G_{123,4}^{(1)sym} = \frac{1}{4}(G_{123,4}^{(1)} + G_{213,4}^{(1)} + G_{312,4}^{(1)} + G_{321,4}^{(1)}) \quad (5.4.33)$$

in the form

$$\begin{aligned} G_{123,4}^{(1)sym} = & -\hbar^2 [\Gamma_3 P_{12} \Gamma_1 (G_{2,134} + G_{4,123}^{t.c.}) \\ & + (\Gamma_1 \Gamma_2 + \frac{1}{4})(G_{3,124} + G_{4,123}^{t.c.})] . \end{aligned} \quad (5.4.34)$$

The right-hand sides of (5.4.34) and (5.4.22) have analogous structures.

5.4.4 Dissipationally Determinable Part of the Biadmittance

The second derivative with respect to the external forces appears in the biadmittance (5.4.1). We have

$$\frac{\delta^2(\hat{B}_1 \hat{B}_2)}{\delta h_3 \delta h_4} = \frac{\delta^2 \hat{B}_1}{\delta h_3 \delta h_4} \hat{B}_2 + \frac{\delta \hat{B}_1}{\delta h_3} \frac{\delta \hat{B}_2}{\delta h_4} + \frac{\delta \hat{B}_1}{\delta h_4} \frac{\delta \hat{B}_2}{\delta h_3} + B_1 \frac{\delta^2 \hat{B}_2}{\delta h_3 \delta h_4} . \quad (5.4.35)$$

We now evaluate the second derivative appearing in the first term. Using (5.2.53) for $t_1 > t_2 > t_3$ we have

$$\frac{\delta^2 \hat{B}_1}{\delta h_3 \delta h_4} = \left(\frac{i}{\hbar}\right)^2 [[\hat{B}_1, \hat{B}_3], \hat{B}_4] . \quad (5.4.36)$$

Also, taking into account the possibility of the inequality $t_1 > t_4 > t_3$, for which an expression analogous to (5.4.36) is valid, we obtain the general formula

$$\frac{\delta^2 \hat{B}_1}{\delta h_3 \delta h_4} = \left(\frac{i}{\hbar}\right)^2 \{\eta_{134} [[\hat{B}_1, \hat{B}_3], \hat{B}_4] + \eta_{143} [[\hat{B}_1, \hat{B}_4], \hat{B}_3]\} , \quad (5.4.37)$$

This formula holds for any t_1, t_3, t_4 . We can write the second derivative in the last term on the right-hand side of (5.4.35) in the same way. Evaluating the first derivatives by using (5.2.50), from (5.4.35) we have

$$\begin{aligned} \left(\frac{\hbar}{i}\right)^2 \left\langle \frac{\delta^2(\hat{B}_1 \hat{B}_2)}{\delta h_3 \delta h_4} \right\rangle = & P_{34} \{\eta_{134} \langle [[\hat{B}_1, \hat{B}_3], \hat{B}_4] \hat{B}_2 \rangle \\ & + \eta_{13} \eta_{24} \langle [\hat{B}_1, \hat{B}_3] [\hat{B}_2, \hat{B}_4] \rangle \\ & + \eta_{234} \langle \hat{B}_1 [[\hat{B}_2, \hat{B}_3], \hat{B}_4] \rangle\} . \end{aligned} \quad (5.4.38)$$

Here we should set $h(t) \equiv 0$. Then the equilibrium mean values will appear on the right-hand side. On using (5.2.78) and setting $\hat{D} = [[\hat{B}_i, \hat{B}_j], \hat{B}_k]$, we find

$$\langle [[\hat{B}_1, \hat{B}_3], \hat{B}_4] \hat{B}_2 \rangle_0 = \Gamma_{134}^+ \langle [[[\hat{B}_1, \hat{B}_3], \hat{B}_4], \hat{B}_2] \rangle_0 = -\Gamma_2^- V_{1342} , \quad (5.4.39a)$$

$$\langle \hat{B}_1 [[\hat{B}_2, \hat{B}_3], \hat{B}_4] \rangle_0 = -\Gamma_1^+ V_{2341} . \quad (5.4.39b)$$

We now express the mean values of the type $\langle [\hat{B}_1, \hat{B}_3][\hat{B}_2, \hat{B}_4] \rangle_0$ in terms of V_{1234} . On using again (5.2.78), and setting $\hat{D} = [\hat{B}_1, \hat{B}_3]$, we have

$$\langle [\hat{B}_1, \hat{B}_3][\hat{B}_2, \hat{B}_4] \rangle_0 = \Gamma_{13}^+ \langle [[\hat{B}_1, \hat{B}_3], [\hat{B}_2, \hat{B}_4]] \rangle_0 . \quad (5.4.40)$$

The double commutator has the property

$$[[\hat{A}, \hat{C}], \hat{D}] + [[\hat{C}, \hat{D}], \hat{A}] + [[\hat{D}, \hat{A}], \hat{C}] = 0 \quad (5.4.41)$$

(see (5.3.52b)). Therefore,

$$\begin{aligned} \langle [[\hat{B}_1, \hat{B}_3], [\hat{B}_2, \hat{B}_4]] \rangle_0 &= -\langle [[[\hat{B}_3, [\hat{B}_2, \hat{B}_4]], \hat{B}_1]] \rangle_0 \\ &\quad - \langle [[[[\hat{B}_2, \hat{B}_4], \hat{B}_1], \hat{B}_3]] \rangle_0 \\ &= V_{2431} - V_{2413} . \end{aligned} \quad (5.4.42)$$

By virtue of (5.4.39, 40, 42) we obtain from (5.4.38)

$$\begin{aligned} &-\hbar^2 [\partial^2 \langle \hat{B}_1 \hat{B}_2 \rangle / \partial h_3 \partial h_4]_{h=0} \\ &= P_{34} [-\eta_{134} \Gamma_2^- V_{1342} - \eta_{234} \Gamma_1^+ V_{2341} + \eta_{13} \eta_{24} \Gamma_{13}^+ (V_{2431} - V_{2413})] . \end{aligned} \quad (5.4.43)$$

Here we can write $-\hbar^2 G_{12,34}$ on the left-hand side because of the presence of Γ^\pm (see below). In (5.4.43) η and Γ^\pm commute. One should note that η_{13} and Γ_{13}^\pm commute since the time difference $t_1 - t_3$ appears in η_{13} and the operator $\partial/\partial t_1 + \partial/\partial t_3$ appears in Γ_{13}^\pm . It is easy to verify that $t_1 - t_3$ and $\partial/\partial t_1 + \partial/\partial t_3$ commute. As a result, we transform (5.4.43) to the form

$$\begin{aligned} \hbar^2 G_{12,34} &= P_{34} \{ \Gamma_2^- (\eta_{134} V_{1342}) + \Gamma_1^+ (\eta_{234} V_{2341}) \\ &\quad - \Gamma_{13}^+ [\eta_{13} \eta_{24} (V_{2431} - V_{2413})] \} . \end{aligned} \quad (5.4.44)$$

In view of (5.4.7), the last term in the braces may be written as follows: $\Gamma_{24}^- \eta_{13} \eta_{24} (V_{1324} - V_{1342})$.

Substituting (5.4.9) into (5.4.44), we obtain the biadmittance in the form of a sum of dissipationally determinable and dissipationally undeterminable parts, i.e.

$$G_{12,34} = G_{12,34}^{(1)} + G_{12,34}^{(2)}, \quad (5.4.45)$$

where

$$\begin{aligned} \hbar^2 G_{12,34}^{(j)} &= P_{34} [\Gamma_2^- \eta_{134} V_{1342}^{(j)} + \Gamma_1^+ \eta_{234} V_{2341}^{(j)} \\ &\quad + \Gamma_{24}^- \eta_{13} \eta_{24} (V_{1324}^{(j)} - V_{1342}^{(j)})] . \end{aligned} \quad (5.4.46)$$

For determining $G_{12,34}^{(1)}$ we have to substitute (5.4.15) or (5.4.30) into equation (5.4.46) with $j = 1$. It is easy to see that the term with $\eta_{24} (V_{2431}^{(1)} - V_{2413}^{(1)})$ vanishes. Therefore we get

$$G_{12,34}^{(1)} = i\hbar P_{34} (\Gamma_2^- \eta_{34} G_{1,234} + \Gamma_1^+ \eta_{34} G_{2,134}), \quad (5.4.47)$$

or

$$G_{12,34}^{(1)} = i\hbar (\Gamma_2^- G_{1,234} + \Gamma_1^+ G_{2,134}). \quad (5.4.48)$$

Here we have used the fact that $\eta_{123} G_{2,134}^{t.c.} = 0$ since $\eta_{321} G_{2,134} = 0$. If in (5.4.48) we perform a symmetrization in the subscripts 1 and 2, we arrive at

$$(G_{12,34}^{(1)})^{\text{sym}} = \frac{1}{2}(G_{12,34}^{(1)} + G_{21,34}^{(1)}) = i\hbar(\Gamma_2 G_{1,234} + \Gamma_1 G_{2,134}). \quad (5.4.49)$$

Thus, the dissipationally determinable part of the biadmittance has been found.

We note that in the last two sections we have substituted the derivatives of correlators for derivatives of moments. This replacement is justifiable for the following reason. Since $\langle \hat{B}_1 \hat{B}_2 \rangle = \langle \hat{B}_1 \hat{B}_2 \rangle + \langle \hat{B}_1 \rangle \langle \hat{B}_2 \rangle$, the difference between $\partial^2 \langle \hat{B}_1 \hat{B}_2 \rangle / \partial h_3 \partial h_4$ and $\partial^2 \langle \hat{B}_1, \hat{B}_2 \rangle / \partial h_3 \partial h_4$ is

$$\begin{aligned} & (\partial^2 \langle \hat{B}_1 \rangle / \partial h_3 \partial h_4) \langle \hat{B}_2 \rangle + P_{34}(\partial \langle \hat{B}_1 \rangle / \partial h_3)(\partial \langle \hat{B}_2 \rangle / \partial h_4) \\ & + \langle \hat{B}_1 \rangle \partial^2 \langle \hat{B}_2 \rangle / \partial h_3 \partial h_4. \end{aligned} \quad (5.4.50)$$

However, the operators $\Gamma_1^+, \Gamma_2^-, \Gamma_{13}^+, \Gamma_{14}^-$, whose properties are analogous to the properties of integration operators $p_1^{-1}, p_2^{-1}, (p_1 + p_3)^{-1}, (p_1 + p_4)^{-1}$, respectively, appear in (5.4.44). Therefore, “constants of integration”, i.e. arbitrary functions $\varphi_1(t_{23}, t_{24}), \varphi_2(t_{13}, t_{14}), \varphi_3(t_{13}, t_{24}), \varphi_4(t_{14}, t_{23})$, can be added to the right-hand side of (5.4.44). The function (5.4.50) belongs to the class of admissible arbitrary functions. Therefore we may write either of the functions $[\partial^2 \langle \hat{B}_1 \hat{B}_2 \rangle / \partial h_3 \partial h_4]_0$ and $G_{12,3}$ on the right-hand side of (5.4.44). The justification for replacing $\delta \langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \rangle / \partial h_4$ by $\delta \langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle / \partial h_4$ and vice versa in (5.4.27) is analogous.

5.4.5 Two Relationships for the Dissipationally Undeterminable Part of the Biadmittance

From (5.4.11) we have

$$P_{23}\eta_{123}V_{1234}^{(2)} = P_{23}[\tilde{b}_{4123} + c_{1243} + (\tilde{c} + \tilde{d})_{1423}] \equiv M_{1423}, \quad (5.4.51a)$$

$$\begin{aligned} \eta_{12}\eta_{34}(V_{1234}^{(2)} - V_{1243}^{(2)}) &= -(b + \tilde{c} + \tilde{d})_{1324} - (\tilde{b} + c + d)_{3142} - (b + \tilde{b})_{3124} \\ & - (d + \tilde{d})_{1342} - c_{1234} - \tilde{c}_{3412} \equiv N_{1324}. \end{aligned} \quad (5.4.51b)$$

These expressions are the definitions of the functions M_{1423} and N_{1324} , respectively. Using (5.4.51), formula (5.4.46) for $j = 2$ can be written as

$$\hbar^2 G_{12,34}^{(2)} = \Gamma_2^- M_{1234} + \Gamma_1^+ M_{2134} + \Gamma_{24}^- N_{1234} + \Gamma_{23}^- N_{1243}. \quad (5.4.52)$$

Expressing the functions M and N in terms of partial functions $b, c, d, \tilde{b}, \tilde{c}, \tilde{d}$ according to (5.4.51), and using (5.4.12), we can easily verify that the functions M and N have the properties:

$$M_{1234} = M_{1243}, \quad (5.4.53a)$$

$$N_{1234} = -N_{2143}, \quad (5.4.53b)$$

$$M_{1234} + M_{3412}^{t.c.} = -N_{1234}. \quad (5.4.53c)$$

From (5.4.53c) we find

$$N_{1234}^{t.c.} = N_{3412}. \quad (5.4.54)$$

Substituting $M_{3412}^{\text{t.c.}} = -M_{1234} - N_{1234}$ into the equation $M_{3412}^{\text{t.c.}} = M_{3421}^{\text{t.c.}}$, which follows from (5.4.53a), we get

$$M_{1234} + N_{1234} - M_{2134} - N_{2134} = 0 \quad (5.4.55)$$

or, if we use (5.4.53b),

$$M_{1234} - M_{2134} + N_{1234} + N_{1243} = 0. \quad (5.4.56)$$

Further, using (5.4.51, 12), we can convince ourselves that the function

$$\begin{aligned} U_{1234} \equiv \eta_{12} V_{1234}^{(2)} &= \tilde{b}_{4132} - b_{1324} - b_{3124} + \tilde{b}_{4123} + c_{1243} - \tilde{c}_{3412} \\ &\quad + \tilde{d}_{1432} - d_{1342} - (c+d)_{3142} + (\tilde{c}+\tilde{d})_{1423} \end{aligned} \quad (5.4.57)$$

can be expressed in terms of the functions (5.4.51) as follows:

$$U_{1234} = M_{1234} + M_{1423} + N_{1324}. \quad (5.4.58)$$

It is easy to prove that the dissipationally undeterminable part of the biadmittance satisfies the relation

$$G_{12,34}^{(2)} = G_{21,34}^{(2)}. \quad (5.4.59)$$

In fact, using (5.4.52, 53b) and (5.2.103), we arrive at

$$\hbar^2(G_{12,34}^{(2)} - G_{21,34}^{(2)}) = -M_{1234} + M_{2134} - N_{1234} - N_{1243}. \quad (5.4.60)$$

Formula (5.4.60) implies (5.4.59) by virtue of (5.4.56).

The second relation for $G_{12,34}^{(2)}$ has the form

$$\Gamma_3^- \Gamma_4^- G_{12,34}^{(2)\text{t.c.}} = \Gamma_1^+ \Gamma_2^+ G_{34,12}^{(2)}. \quad (5.4.61)$$

To prove (5.4.61), we substitute (5.4.52) into its left-hand side and transform the resulting expression such that the operator Γ_1^+ appears in each term. For this purpose we have to use (5.2.110) and the identity (5.2.105), i.e. the equation

$$\begin{aligned} \Gamma_2^- \Gamma_3^- \Gamma_4^- &= -\Gamma_1^+(\Gamma_3^- \Gamma_4^- + \Gamma_2^+ \Gamma_4^- + \Gamma_2^+ \Gamma_3^+) \\ \text{for } p_1 + p_2 + p_3 + p_4 &= 0. \end{aligned} \quad (5.4.62)$$

Then the terms with $\Gamma_1^+ \Gamma_3^- \Gamma_4^-$ cancel out. As a consequence of (5.4.56) we obtain

$$\begin{aligned} \Gamma_3^- \Gamma_4^- G_{12,34}^{(2)\text{t.c.}} &= -\Gamma_1^+ \Gamma_2^+ [\Gamma_4^-(M_{1234} + N_{1234})^{\text{t.c.}} + \Gamma_3^+ M_{1234}^{\text{t.c.}} \\ &\quad + (\Gamma_4^- + \Gamma_{13}^+) N_{1234}^{\text{t.c.}} + (\Gamma_3^- + \Gamma_{14}^+) N_{1243}^{\text{t.c.}}]. \end{aligned} \quad (5.4.63)$$

Here we may take $\Gamma_3^- + \Gamma_{14}^+$ instead of $\Gamma_3^+ + \Gamma_{14}^-$. Substituting (5.4.52) into the right-hand side of (5.4.61) and comparing the resulting expression with (5.4.63), we can easily prove (5.4.61) if we use (5.4.53b, c, 54).

The relation (5.4.61) may be written in another form. Multiplying (5.4.61) by $\exp[i\beta\hbar(p_3 + p_4)/2] = \exp[-i\beta\hbar(p_1 + p_2)/2]$ and using the definition of the operators Γ^\pm , we readily obtain

$$\Gamma'_3 \Gamma'_4 G_{12,34}^{(2)\text{t.c.}} = \Gamma'_1 \Gamma'_2 G_{34,12}^{(2)}, \quad (5.4.64)$$

where

$$\Gamma'(p) = (\Gamma^+ \Gamma^-)^{1/2} = [2\text{sh}(\frac{1}{2}\text{i}\beta\hbar p)]^{-1}. \quad (5.4.65)$$

If we substitute

$$\begin{aligned} G_{12,34}^{(2)} &= G_{12,34} - G_{12,34}^{(1)} \\ &= G_{12,34} - i\hbar(\Gamma_2^- G_{1,234} + \Gamma_1^+ G_{2,134}), \end{aligned} \quad (5.4.66)$$

where (5.4.48) has been used, or the symmetrized expression

$$G_{12,34}^{(2)} = G_{12,34}^{\text{sym}} - i\hbar(\Gamma_2 G_{1,234} - \Gamma_1 G_{2,134}) \quad (5.4.67)$$

into (5.4.59, 61) or (5.4.64), we obtain equations for the total biadmittance $G_{12,34}$ or for its symmetrized variant $G_{12,34}^{\text{sym}} = \frac{1}{2}(G_{12,34} + G_{21,34})$.

5.4.6 Relations for the Dissipationally Undeterminable Part of the Triadmittance

The functions $G_{12,34}^\pm$ are defined by

$$\begin{aligned} \hbar^2 G_{12,34}^{-(2)} &= \Gamma_2^- M_{1234} + \Gamma_{24}^- N_{1234}, \\ \hbar^2 G_{12,34}^{+(2)} &= \Gamma_2^+ M_{1234} + \Gamma_{24}^+ N_{1234}. \end{aligned} \quad (5.4.68)$$

Using these, we can write (5.4.52) as

$$G_{12,34}^{(2)} = G_{12,34}^{-(2)} + G_{21,34}^{+(2)}. \quad (5.4.69)$$

Let us prove that

$$G_{123,4}^{(2)} = i\hbar(\Gamma_3^- G_{12,34}^{(2)} + \Gamma_2^- G_{13,24}^{(2)} + \Gamma_2^+ G_{31,24}^{(2)} + \Gamma_1^+ G_{23,14}^{(2)}). \quad (5.4.70)$$

Employing (5.4.29) with $j = 2$ and using the definition (5.4.57), we have

$$\begin{aligned} G_{123,4}^{(2)} &= (i/\hbar)[\Gamma_{23}^-(\Gamma_3^- U_{1423} + \Gamma_2^+ U_{1432}) + \Gamma_{13}^+ \Gamma_3^- U_{2413} \\ &\quad + \Gamma_{13}^- \Gamma_1^+ U_{2431} + \Gamma_{12}^+(\Gamma_2^- U_{3412} + \Gamma_1^+ U_{3421})]. \end{aligned} \quad (5.4.71)$$

On the other hand, we substitute (5.4.69, 68) into the right-hand side of (5.4.70). Then we use (5.2.107) in order to have only operator products of the type $\Gamma_k^\pm \Gamma_{kl}^\pm$ instead of $\Gamma_k^\pm \Gamma_l^\pm$. Further, using (5.2.103), we transform all products of the type $\Gamma_k^\pm \Gamma_{lm}^\pm$ into products of the type $\Gamma_k^\pm \Gamma_{kl}^\pm$. We are left with only the following products: $\Gamma_3^- \Gamma_{23}^-$, $\Gamma_2^+ \Gamma_{23}^-$, $\Gamma_3^- \Gamma_{13}^+$, $\Gamma_1^+ \Gamma_{13}^-$, $\Gamma_1^+ \Gamma_{12}^+$, $\Gamma_2^- \Gamma_{12}^+$, i.e. the same ones as in (5.4.71). As a consequence of (5.4.58) the multipliers appearing behind $\Gamma_3^- \Gamma_{23}^-$, $\Gamma_2^+ \Gamma_{23}^-$, etc. on the right-hand side of (5.4.70) are equal to the corresponding multipliers on the right-hand side of (5.4.71). Therefore, (5.4.70) is valid.

In the nonquantum limit we obtain from (5.4.70)

$$G_{123,4}^{(2)} = kT(p_3^{-1} G_{12,34}^{(2)} + p_2^{-1} G_{13,24}^{(2)} + p_1^{-1} G_{23,14}^{(2)}). \quad (5.4.72)$$

Hence we see that the triadmittance is expressed in terms of the biadmittance and the ordinary admittance in the nonquantum case. In the quantum case we are unable to express the triadmittance in terms of the admittance and the biadmittance. Combining (5.4.69) with (5.4.70), we can only express $G_{12,34}^\pm$ in terms of

$G_{12,34}^{(2)}$ and $G_{123,4}^{(2)}$:

$$\begin{aligned} G_{13,24}^{(2)} &= (i/\hbar)G_{123,4}^{(2)} + \Gamma_3^- G_{12,34}^{(2)} + \Gamma_2^+ G_{13,24}^{(2)} + \Gamma_1^+ G_{23,14}^{(2)}, \\ G_{31,24}^{(2)} &= - (i/\hbar)G_{123,4}^{(2)} - \Gamma_3^- G_{12,34}^{(2)} - \Gamma_2^- G_{13,24}^{(2)} - \Gamma_1^+ G_{23,14}^{(2)}. \end{aligned} \quad (5.4.73)$$

If $G_{123,4}^{(2)}$ and $G_{12,34}^{(2)}$ are known, we can find not only $G_{12,34}^{\pm(2)}$ but also the functions M_{1234} and N_{1234} , which appear in (5.4.68). In fact, (5.4.68) can be regarded as a system of linear equations in M_{1234} and N_{1234} . The system is nondegenerate in the quantum case. Solving it, we easily find

$$\begin{aligned} M_{1234} &= \hbar^2 \Delta^{-1} (\Gamma_{24}^+ G_{12,34}^{(2)} - \Gamma_{24}^- G_{12,34}^{(2)}), \\ N_{1234} &= \hbar^2 \Delta^{-1} (\Gamma_2^- G_{12,34}^{(2)} - \Gamma_2^+ G_{12,34}^{(2)}), \end{aligned} \quad (5.4.74)$$

where $\Delta = \Gamma_2^- - \Gamma_{24}^-$. If we now substitute (5.4.73) into (5.4.74) and then the result into (5.4.53), we get a number of relationships between the triadmittance $G_{123,4}$, the biadmittance $G_{12,34}$ and the admittance $G_{1,234}$ (if we use complete functions (5.4.45, 28)).

5.4.7 Relations for the Dissipationally Undeterminable Part of the Quadruple Equilibrium Correlator

The dissipationally undeterminable part of the equilibrium correlator is defined by (5.4.17) with $j = 2$. We have $V_{1234}^{(2)} = (\eta_{12} + \eta_{21})V_{1234} = \eta_{12}V_{1234}^{(2)} - \eta_{21}V_{2134}^{(2)}$. We can therefore express the function $V_{1234}^{(2)}$ in terms of the function (5.4.57): $V_{1234}^{(2)} = U_{1234} - U_{2134}$. Taking this into account, we find from (5.4.17)

$$\begin{aligned} G_{1234}^{(2)} &= \Gamma_1^+ [\Gamma_4^- \Gamma_{34}^- (U_{1234} - U_{2134}) + \Gamma_3^+ \Gamma_{34}^- (U_{1243} - U_{2143}) \\ &\quad + \Gamma_4^- \Gamma_{24}^+ (U_{1324} - U_{3124}) + \Gamma_2^+ \Gamma_{24}^- (U_{1342} - U_{3142}) \\ &\quad + \Gamma_3^- \Gamma_{23}^+ (U_{1423} - U_{4123}) + \Gamma_2^+ \Gamma_{23}^+ (U_{1432} - U_{4132})]. \end{aligned} \quad (5.4.75)$$

Let us introduce the functions

$$\hbar^2 C_{1234}^{\pm} = \Gamma_2^{\pm} M_{1234}, \quad \hbar^2 D_{1234} = \Gamma_{24}^- N_{1234}, \quad (5.4.76)$$

so that (5.4.68) takes the form

$$\begin{aligned} G_{12,34}^{(2)} &= C_{1234}^- + D_{1234}, \\ G_{12,34}^{(2)} &= C_{1234}^+ + D_{2143} \end{aligned} \quad (5.4.77)$$

($D_{2143} = \Gamma_{13}^- N_{2143} = -\Gamma_{24}^+ N_{2143}$ coincides with $\Gamma_{24}^+ N_{1234}$ by virtue of (5.4.53b)).

One can prove that

$$\begin{aligned} G_{1234}^{(2)} &= (i\hbar)^2 [\Gamma_3^- \Gamma_4^- G_{12,34}^{(2)} + \Gamma_4^- (\Gamma_2^- G_{13,24}^{(2)} + \Gamma_2^+ G_{31,24}^{(2)}) \\ &\quad + \Gamma_2^- \Gamma_3^- C_{1423}^- + \Gamma_2^+ \Gamma_3^+ C_{4123}^+ + \Gamma_2^- \Gamma_3^+ D_{1423} + \Gamma_2^+ \Gamma_3^- D_{1432} \\ &\quad + \Gamma_1^+ \Gamma_4^- G_{23,14}^{(2)} + \Gamma_1^+ (\Gamma_3^- G_{24,31}^{(2)} + \Gamma_3^+ G_{42,31}^{(2)}) + \Gamma_1^+ \Gamma_2^+ G_{34,12}^{(2)}]. \end{aligned} \quad (5.4.78)$$

In order to verify this, we substitute (5.4.75) into the left-hand side of (5.4.78) and (5.4.52, 68, 76) into the right-hand side of (5.4.78). Then we insert (5.4.62) and (5.2.110, 111) (and also the analogous equations with a permutation of the subscripts 2, 3, 4) into the right-hand side of (5.4.78) so that the operator Γ_1^+ appears in all the terms, and thus we can cancel Γ_1^+ . Further, using (5.2.107), the products of operators of the type $\Gamma_k^\pm \Gamma_1^\pm$ can be replaced by a sum of products of the type $\Gamma_k^\pm \Gamma_{kl}^\pm$ in all the terms. We also perform a transformation of the type $\Gamma_4^- \Gamma_{13}^- \rightarrow -\Gamma_4^- \Gamma_{42}^+$ to the form $\Gamma_k^\pm \Gamma_{kl}^\pm$ in the terms in which products of the type $\Gamma_k^\pm \Gamma_{lm}^\pm$ have the subscript k that coincides with neither l nor m . Finally, using equations $\Gamma^\pm = \Gamma^\mp \pm 1$, we pass on to the following operator products: $\Gamma_4^- \Gamma_{34}^-$, $\Gamma_3^+ \Gamma_{34}^-$, $\Gamma_4^- \Gamma_{24}^+$, $\Gamma_2^+ \Gamma_{24}^-$, $\Gamma_3^- \Gamma_{23}^+$, $\Gamma_2^+ \Gamma_{23}^+$. We can now compare the multipliers appearing behind these products on both sides of the equation. The calculations show that the functions on the left-hand side of (5.4.78) are equal to the functions on its right-hand side by virtue of (5.4.58). Equation (5.4.78) is therefore valid.

In the nonquantum limit we obtain from (5.4.78)

$$\begin{aligned} G_{1234}^{(2)} &= (kT)^2 (p_3^{-1} p_4^{-1} G_{12,34}^{(2)} + p_2^{-1} p_4^{-1} G_{13,24}^{(2)} + p_2^{-1} p_3^{-1} G_{14,23}^{(2)} \\ &\quad + p_1^{-1} p_4^{-1} G_{23,14}^{(2)} + p_1^{-1} p_3^{-1} G_{24,31}^{(2)} + p_1^{-1} p_2^{-1} G_{34,12}^{(2)}). \end{aligned} \quad (5.4.79)$$

Consequently, in the nonquantum case $G_{1234}^{(2)}$ can be expressed in terms of $G_{12,34}^{(2)}$ or $G_{12,34}$ and $G_{1,234}$ unlike the quantum case.

In the quantum case $G_{1234}^{(2)}$ can be expressed only in terms of $G_{12,34}^{(2)}$ and $G_{123,4}^{(2)}$. Let us show how one can do this. As a consequence of (5.4.76, 74) we have

$$D_{1234} = (\Gamma_2^- - \Gamma_{24}^-)^{-1} \Gamma_{24}^- \Gamma_2^+ (E_2^{-1} G_{12,34}^{(2)} - G_{12,34}^{(2)}), \quad (5.4.80)$$

where $E_2 = \Gamma_2^+ / \Gamma_2^- = \exp(i\beta\hbar p_2)$. Using (5.2.107), equation (5.4.80) can be somewhat simplified, i.e.

$$D_{1234} = \Gamma_4^- (E_2^{-1} G_{12,34}^{(2)} - G_{12,34}^{(2)}). \quad (5.4.81)$$

We can also obtain another expression for D_{1234} . Taking into account the property $N_{1234} = -N_{2143}$, we find from (5.4.76) $\hbar^2 D_{1234} = -\Gamma_{24}^- N_{2143} = \Gamma_{13}^+ N_{2143}$. Hence by virtue of (5.4.74) we obtain

$$\begin{aligned} D_{1234} &= (\Gamma_1^- - \Gamma_{13}^-)^{-1} \Gamma_{13}^+ \Gamma_1^- (G_{21,43}^{(2)} - E_1 G_{21,43}^{(2)}) \\ &= \Gamma_3^+ (G_{21,43}^{(2)} - E_1 G_{21,43}^{(2)}). \end{aligned} \quad (5.4.82)$$

The terms

$$\begin{aligned} &\Gamma_2^- \Gamma_3^- C_{1423}^- + \Gamma_2^+ \Gamma_3^+ C_{4123}^+ + \Gamma_2^- \Gamma_3^+ D_{1423} + \Gamma_2^+ \Gamma_3^- D_{1432} \\ &= \Gamma_2^- \Gamma_3^- G_{14,23}^{(2)} + \Gamma_2^+ \Gamma_3^+ G_{41,23}^{(2)} + \Gamma_2^- D_{1423} - \Gamma_2^+ D_{1432} \end{aligned} \quad (5.4.83)$$

appear in (5.4.78). Here (5.4.77) has been used.

We now substitute an expression of the type (5.4.81) for D_{1423} and an expression of the type (5.4.82) for D_{1432} into (5.4.83). After cancellations we have

$$(5.4.83) = E_4^- \Gamma_2^- \Gamma_3^- G_{14,23}^{(2)} + E_1 \Gamma_2^+ \Gamma_3^+ G_{41,23}^{(2)} = E_1 \Gamma_2^+ \Gamma_3^+ G_{41,23}^{(2)} \quad (5.4.84)$$

(see (5.4.69)). Therefore, (5.4.78) can be written in the form

$$\begin{aligned} G_{1234}^{(2)} = & -\hbar^2 [\Gamma_3^- \Gamma_4^- G_{12,34}^{(2)} + \Gamma_4^- (\Gamma_2^- G_{13,24}^{(2)} + \Gamma_2^+ G_{31,24}^{(2)}) + E_1 \Gamma_2^+ \Gamma_3^+ G_{41,23}^{(2)} \\ & + \Gamma_1^+ \Gamma_4^- G_{23,14}^{(2)} + \Gamma_1^+ (\Gamma_3^- G_{24,31}^{(2)} + \Gamma_3^+ G_{42,31}^{(2)}) + \Gamma_1^+ \Gamma_2^+ G_{34,12}^{(2)}] . \end{aligned} \quad (5.4.85)$$

Using (5.4.70), this may also be written as

$$G_{1234}^{(2)} = i\hbar(\Gamma_4^- G_{12,34}^{(2)} + \Gamma_1^+ G_{23,14}^{(2)}) + \hbar^2(\Gamma_1^+ \Gamma_4^- G_{23,14}^{(2)} - E_1 \Gamma_2^+ \Gamma_3^+ G_{41,23}^{(2)}) . \quad (5.4.86)$$

Both the equilibrium correlator G_{1234} and the moment $\langle \hat{B}_1 \hat{B}_2 \hat{B}_3 \hat{B}_4 \rangle_0$ have the properties

$$G_{1234} = E_1 G_{2341} , \quad (5.4.87a)$$

$$G_{1234}^{\text{t.c.}} = G_{1234} \quad (5.4.87b)$$

[(5.4.87a) follows from (5.2.71)]. Using (5.4.20), we easily verify that the dissipationally determinable part has identical properties. Therefore (5.4.87) implies

$$\begin{aligned} G_{1234}^{(2)} &= E_1 G_{2341}^{(2)} \\ G_{1234}^{(2)\text{t.c.}} &= G_{1243}^{(2)} . \end{aligned} \quad (5.4.88)$$

Substituting (5.4.86) into (5.4.88), we can find relationships between the functions $G_{12,34}^{(2)}$ and $G_{12,34}^{(2)}$ and, consequently, those between $G_{123,4}$, $G_{12,34}$ and $G_{1,234}$. For example, (5.4.87a) yields

$$\begin{aligned} \Gamma_4^- G_{123,4}^{(2)} - E_1 \Gamma_2^+ G_{341,2}^{(2)} \\ = i\hbar(\Gamma_3^- \Gamma_4^- G_{12,34}^{(2)} + \Gamma_1^+ \Gamma_4^- G_{23,14}^{(2)} - \Gamma_1^+ \Gamma_2^+ G_{34,21}^{(2)} - E_1 \Gamma_2^+ \Gamma_3^+ G_{41,23}^{(2)}) . \end{aligned} \quad (5.4.89)$$

The relation connecting $G_{123,4}$, $G_{12,34}$ and $G_{1,234}$ is easily obtained from (5.4.89).

Thus, in the general case, the dissipationally undeterminable part $G_{1234}^{(2)}$ is expressed in terms of $G_{123,4}^{(2)}$ and $G_{12,34}^{(2)}$ according to (5.4.86). Consequently, G_{1234} is expressed in terms of $G_{123,4}$, $G_{12,34}$ and $G_{1,234}$. Moreover, there exist relationships connecting the last three functions.

5.4.8 Using Symmetrized Triadmittance for Obtaining the Quadruple Correlator

The quadruple correlator G_{1234} can be also expressed in terms of the functions $G_{123,4}^s$, $G_{12,34}$ and $G_{1,234}$, where

$$G_{123,4}^s = \frac{1}{2}(G_{123,4} + G_{321,4}) \quad (5.4.90)$$

is the symmetrized triadmittance. Let us show this.

Since $\Gamma^\pm = \Gamma \pm 1/2$, equation (5.4.70) can be written as

$$(i\hbar)^{-1} G_{123,4}^{(2)} = \Gamma_3^- G_{12,31}^{(2)} + \Gamma_1^+ G_{23,14}^{(2)} + \Gamma_2 G_{13,24}^{(2)} - \frac{1}{2}(G_{13,24}^{(2)} - G_{31,24}^{(2)}) . \quad (5.4.91)$$

Using this we easily obtain

$$(2i\hbar)^{-1}(G_{123,4}^{(2)} + G_{321,4}^{(2)}) = \Gamma_3 G_{12,34}^{(2)} + \Gamma_1 G_{23,14}^{(2)} + \Gamma_2 G_{13,24}^{(2)} + \frac{1}{4}P_{13}(G_{13,24}^{(2)} - G_{13,24}^{(2)}). \quad (5.4.92)$$

Thus, the dissipationally undeterminable part of the symmetrized triadmittance (5.4.90) has been found. It is convenient to introduce the function

$$\begin{aligned} R_{1324} &= \frac{1}{2}(G_{123,4}^{(2)} + G_{321,4}^{(2)}) - i\hbar(\Gamma_3 G_{12,34}^{(2)} + \Gamma_2 G_{13,24}^{(2)} + \Gamma_1 G_{23,14}^{(2)}) \\ R_{1324} &= R_{3124}. \end{aligned} \quad (5.4.93)$$

By using (5.4.68), the difference between the functions $G^{\pm(2)}$ appearing in (5.4.92) can be expressed in terms of functions N and M . We obtain

$$\hbar^2(G_{12,34}^{(2)} - G_{12,34}^{(2)}) = M_{1234} + N_{1234}. \quad (5.4.94)$$

Hence, using (5.4.55), we find

$$\hbar^2 P_{12}(G_{12,34}^{(2)} - G_{12,34}^{(2)}) = 2(M_{1234} + N_{1234}). \quad (5.4.95)$$

By virtue of (5.4.53c) the expression on the right-hand side of (5.4.95) is also equal to $-2M_{3412}^{t.c.}$. Thus, using (5.4.93), we can write (5.4.92) in the form

$$2i\hbar R_{1234} = M_{3412}^{t.c.}. \quad (5.4.96)$$

Here we have performed a permutation of the subscripts 2 and 3.

Thus, the function M has been expressed in terms of R . Using (5.4.53c), we can also express function N in terms of R :

$$N_{1234} = -2i\hbar(R_{1234} - R_{3412}^{t.c.}). \quad (5.4.97)$$

Consequently, all the dissipationally undeterminable parts of four-subscript functions can be expressed in terms of R_{1234} and $G_{12,34}^{(2)}$.

We now return to the quadruple correlator, which is defined by (5.4.85). Combinations of the type

$$\Gamma_3^- G_{12,34}^{(2)} + \Gamma_3^+ G_{21,34}^{(2)} = \Gamma_3 G_{12,34}^{(2)} - \frac{1}{2}(G_{12,34}^{(2)} - G_{21,34}^{(2)}). \quad (5.4.98)$$

appear in (5.4.85) besides $G_{ij,kl}^{(2)}$. By virtue of (5.4.68) we have

$$\begin{aligned} G_{12,34}^{(2)} - G_{21,34}^{(2)} &= \hbar^{-2}[(\Gamma_2^- - \Gamma_1^+)M_{1234} \\ &\quad + (\Gamma_{24}^- - \Gamma_1^+)N_{1234} + (\Gamma_1^+ - \Gamma_{14}^+)N_{2134}]. \end{aligned} \quad (5.4.99)$$

Substitution of (5.4.96, 97) into (5.4.99) gives the final formula

$$\begin{aligned} \frac{1}{2}(G_{12,34}^{(2)} - G_{21,34}^{(2)}) &= (i\hbar)^{-1}[(\Gamma_{24}^- - \Gamma_{14}^+)R_{1234} - (\Gamma_{24}^- - \Gamma_2^-)R_{3412}^{t.c.} \\ &\quad - (\Gamma_1^+ - \Gamma_{14}^+)R_{3421}^{t.c.}]. \end{aligned} \quad (5.4.100)$$

From (5.4.53c) it is seen that the functions M and N are of the same order of magnitude. Since Γ^\pm have the order of magnitude \hbar^{-1} in the parameter \hbar (more precisely, in the dimensionless parameter $\hbar\omega\beta$), from (5.4.68) we deduce that M has the same order of magnitude as $\hbar^3 G_{12,34}^{\pm(2)}$ or $\hbar^3 G_{12,34}^{(2)} = \hbar^3(G_{12,34}^{(2)} + G_{21,34}^{(2)})$. Therefore, by virtue of (5.4.96) the difference (5.4.93) can be evaluated as follows:

$R_{1234} \sim \hbar^2 G_{12,34}^{(2)}$. Thus, in the zeroth and first orders in \hbar , the equation

$$G_{123,4}^{(2)} + G_{321,4}^{(2)} = 2i\hbar(\Gamma_3 G_{12,34}^{(2)} + \Gamma_2 G_{13,24}^{(2)} + \Gamma_1 G_{32,14}^{(2)}) . \quad (5.4.101)$$

holds. This can be obtained from (5.4.93).

Not any arbitrary function can play the role of the function R in (5.4.100). Firstly, this function must satisfy the relation

$$(R_{1234} + R_{1243})^{t.c.} = R_{3412} + R_{3421} , \quad (5.4.102)$$

which follows from (5.4.96) and (5.4.53c, b). Secondly, according to (5.4.68, 69, 96, 97), the equation

$$(\Gamma_{24} + \Gamma_{14})R_{1234} + (\Gamma_2 - \Gamma_{24})R_{3412}^{t.c.} + (\Gamma_1 - \Gamma_{14})R_{3421}^{t.c.} = \frac{1}{2}i\hbar G_{12,34}^{(2)} \quad (5.4.103)$$

must be valid.

The antisymmetric combination $G_{123,4}^{(2)} - G_{321,4}^{(2)}$ can be expressed in terms of the function R_{1234} . In fact, substituting (5.4.100) into (5.4.91), we find

$$\begin{aligned} \frac{1}{2}(G_{123,4}^{(2)} - G_{321,4}^{(2)}) &= -i\hbar(G_{12,34}^{(2)} + G_{23,14}^{(2)}) - (\Gamma_{34} - \Gamma_{14})R_{1324} \\ &\quad + (\Gamma_{34} - \Gamma_3)R_{2413}^{t.c.} + (\Gamma_1 - \Gamma_{14})R_{2431}^{t.c.} . \end{aligned} \quad (5.4.104)$$

Note that the function (5.4.99) and, consequently, the quadruple correlator $G_{1234}^{(2)}$ can be expressed not only in terms of R_{1234} , but also in terms of the antisymmetric function $G_{123,4}^{(2)} - G_{321,4}^{(2)}$. However, the resulting formulas are more complex in this case.

5.4.9 Modified Cubic FDRs

Modified four-subscript functions are defined as follows:

$$\begin{aligned} Y_{1,234} &= p_1 G_{1,234} , \\ Y_{12,34} &= p_1 p_2 G_{12,34} , \\ Y_{123,4} &= p_1 p_2 p_3 G_{123,4} , \\ Y_{1234} &= p_1 p_2 p_3 p_4 G_{1234} = \langle \hat{J}_1, \hat{J}_2, \hat{J}_3, \hat{J}_4 \rangle_0 . \end{aligned} \quad (5.4.105)$$

Their dissipationally determinable and dissipationally undeterminable parts are defined analogously. Differentiating the relations obtained in Sects. 5.4.2–4, we can readily derive the relationships between these functions. Thus, according to (5.4.20, 32, 48) we have the following expressions for the dissipationally determinable parts:

$$\begin{aligned} Y_{1234}^{(1)} &= (kT)^3 [\Theta_2^- \Theta_3^- \Theta_4^-(Y_{1,234} + Y_{1,234}^{t.c.}) + \Theta_1^+ \Theta_3^- \Theta_4^-(Y_{2,134} + Y_{2,134}^{t.c.}) \\ &\quad + \Theta_1^+ \Theta_2^+ \Theta_4^-(Y_{3,124} + Y_{3,124}^{t.c.}) + \Theta_1^+ \Theta_2^+ \Theta_3^+(Y_{4,123} + Y_{4,123}^{t.c.})] , \end{aligned} \quad (5.4.106a)$$

$$Y_{123,4}^{(1)} = (kT)^2 [\Theta_2^- \Theta_3^- Y_{1,234} + \Theta_1^+ \Theta_3^- Y_{2,134} + \Theta_1^+ \Theta_2^+ Y_{3,124} \\ - (p_1 \Theta_2^- \Theta_3^- + p_2 \Theta_1^+ \Theta_3^- + p_3 \Theta_1^+ \Theta_2^+) p_4^{-1} Y_{4,123}^{t.c.}] , \quad (5.4.106b)$$

$$Y_{12,34}^{(1)} = kT(\Theta_2^- Y_{1,234} + \Theta_1^+ Y_{2,134}) , \quad (5.4.106c)$$

where Θ^\pm have the same sense (5.3.93) as in the relations of Sect. 5.3.7. Furthermore, from (5.4.59, 61, 70, 85) we obtain

$$Y_{12,34}^{(2)} = Y_{21,34}^{(2)}, \quad (5.4.107a)$$

$$\Theta_3^- \Theta_4^- Y_{12,34}^{(2)t.c.} = \Theta_1^+ \Theta_2^+ Y_{34,12}^{(2)}, \quad (5.4.107b)$$

$$Y_{123,4}^{(2)} = kT(\Theta_3^- Y_{12,34}^{(2)} + \Theta_2^- Y_{13,24}^{(2)} + \Theta_2^+ Y_{31,24}^{(2)} + \Theta_1^+ Y_{23,14}), \\ (5.4.107c)$$

$$Y_{1234}^{(2)} = (kT)^2 [\Theta_3^- \Theta_4^- Y_{12,34}^{(2)} + \Theta_4^- (\Theta_2^- Y_{13,24}^{(2)} + \Theta_2^+ Y_{31,24}^{(2)}) \\ + E_1 \Theta_2^+ \Theta_3^+ Y_{41,23}^{(2)} + \Theta_1^+ \Theta_4^- Y_{23,14}^{(2)} \\ + \Theta_1^+ (\Theta_3^- Y_{24,31}^{(2)} + \Theta_3^+ Y_{42,31}^{(2)}) + \Theta_1^+ \Theta_2^+ Y_{34,12}^{(2)}]. \quad (5.4.107d)$$

Here $Y_{12,34}^{\pm(2)} = p_1 p_2 G_{12,34}^{\pm(2)}$. The analogy between the modified formulas and initial ones is obvious. This analogy also holds for the other formulas, which have not been derived here. In the nonquantum limit, the operators Θ^\pm go to unity and, instead of (5.4.107b–d), we have

$$Y_{12,34}^{(2)t.c.} = Y_{34,12}^{(2)} \quad (5.4.108a)$$

$$Y_{123,4}^{(2)} = kTP_{(123)} Y_{12,34}^{(2)}, \quad (5.4.108b)$$

$$Y_{1234}^{(2)} = (kT)^2 P_{(234)} (Y_{12,34}^{(2)} + Y_{42,31}^{(2)}). \quad (5.4.108c)$$

Instead of (5.4.106) we obtain

$$Y_{12,34}^{(1)} = kT(Y_{1,234} + Y_{2,134}), \quad (5.4.109a)$$

$$Y_{123,4}^{(1)} = (kT)^2 (Y_{1,234} + Y_{2,134} + Y_{3,124} + Y_{4,123}^{t.c.}), \quad (5.4.109b)$$

$$Y_{1234}^{(1)} = (kT)^3 P_{(1234)} (Y_{1,234} + Y_{1,234}^{t.c.}). \quad (5.4.109c)$$

Equation (5.4.108a) is the non-Markov analogue of (4.1.27). Adding (5.4.109a) to $Y_{12,34}^{(2)}$, we get the relation

$$Y_{12,34} = kT(Y_{1,234} + Y_{2,134}) + Y_{12,34}^{(2)}, \quad (5.4.110)$$

which is the non-Markov analogue of (4.1.28). The relations for $Y_{123,4}$ and Y_{1234} following from (5.4.108, 109) are the analogues of (4.1.29, 31). We see that all these relations have the same structure although certain terms have different signs. Such uniformity of structure is a characteristic feature of FDRs of the various kinds.

5.5 Connection Between FDRs of the First and Second Kinds

5.5.1 Relaxation Equations with External Forces

In the absence of external forces, the relaxation equations have the form (5.1.1). If the external forces $h_\alpha(t)$ varying in time act on a system, then the relaxation

equations naturally have a more complex form:

$$\dot{A}_\alpha(t) = \chi_\alpha[t, A(\cdot), h(\cdot)]. \quad (5.5.1)$$

Here $\chi_\alpha[t, A(\cdot), h(\cdot)]$ are functionals having the property that $\chi_\alpha[t, A(\cdot), 0]$ coincides with functionals $\chi_\alpha[A(\cdot)]$ appearing in (5.1.1). Consequently, (5.5.1) goes over into (5.1.1) if the external forces are equal to zero. Besides the external forces, we can consider forces $x_\alpha(t)$ that are functions of $A_\alpha(t)$. The transition from A to x is simply an inertialess change of variables. Strictly speaking, the dependence $x(A)$ is the inverse of the dependence

$$A_\alpha(x) = \int B_\alpha w_{\text{eq}}(B) \exp(\beta Bx) dB / \int w_{\text{eq}}(B) \exp(\beta Bx) dB \quad (5.5.2)$$

and can be approximately represented by (3.1.38). Changing variables on the right-hand side of (5.5.1), we obtain equations in the standard form

$$\dot{A}_\alpha = -\Omega_\alpha\{t, x[A(\cdot)], h(\cdot)\}, \quad (5.5.3)$$

which are equivalent to (5.5.1). Here $\Omega_\alpha\{t, x[A(\cdot)], h(\cdot)\} = \chi_\alpha[t, A(\cdot), h(\cdot)]$.

In order that (5.5.3) goes over into (5.1.2) for $h(t) \equiv 0$, the functional $\Omega[x, h]$ must satisfy the condition

$$\Omega_\alpha[x(\cdot), 0] = \Psi_\alpha[x(\cdot)], \quad \alpha = 1, 2, \dots. \quad (5.5.4)$$

Let us indicate another property of the functional in (5.5.3). If the external forces h_α are constant in time, then the equilibrium probability density is

$$w_h(B) = \text{const} \cdot w_{\text{eq}}(B) \exp(-\beta Bh), \quad (5.5.5)$$

which can be obtained from the Gibbs probability density

$$w_h(z) = \text{const} \cdot \exp(-\beta \mathcal{H}(z, h)) = \text{const} \cdot \exp(-\beta \mathcal{H}_0(z) + \beta B(z)h). \quad (5.5.6)$$

Here (5.2.1) has been used. By virtue of (5.5.2) the average $A(h)$ corresponds to the probability density (5.5.5). This average must not vary in time for constant h_α . Consequently, if $A(x) = A(h)$ (i.e. $x = h$), $\dot{A} = 0$, or by virtue of (5.5.3)

$$\Omega_\alpha[h(\cdot), h(\cdot)] = 0, \quad \text{for } h_\beta = \text{const.} \quad \alpha = 1, 2, \dots \quad (5.5.7)$$

must be valid.

If (5.1.2) is known, in the general case we still do not know the form of the equation (5.5.3) in which the forces appear, since the functionals $\Omega_\alpha[x, h]$ are not completely determined by (5.5.4, 7). However, we can put forward the hypothesis that in a sufficiently large number of cases the functionals $\Omega_\alpha[x, h]$ are rather simply defined in terms of the functionals $\Psi_\alpha[x]$:

$$\Omega_\alpha[x(\cdot), h(\cdot)] = \Psi_\alpha[x(\cdot) - h(\cdot)]. \quad (5.5.8)$$

This hypothesis will be called the hypothesis of the simplest inclusion of forces. It is obvious that conditions (5.5.4, 7) will be fulfilled in the case of (5.5.8).

Equation (5.5.8) is a rather strong statement, and we are unable to prove it completely. It will be shown that (5.5.8) is a sufficient condition for deriving the linear and quadratic FDRs of the first kind from the corresponding relations of the second kind.

5.5.2 Derivation of Reciprocal Relation of the First Kind

In the framework of the linear theory, if hypothesis (5.5.8) is invoked, equations (5.5.3) have the form

$$\dot{A}_1 = -\Phi_{1,2}(x_2 - h_2), \quad (5.5.9)$$

where $\Phi_{1,2}$ has the same sense as in (5.1.4). In this approximation $x(A)$ has a linear dependence on A :

$$x_\alpha = u_{\alpha\beta} A_\beta \quad (5.5.10)$$

(see (5.1.8)). Substitution of (5.5.10) into (5.5.9) gives

$$(p_1 \delta_{12} + \Phi_{1,3} U_{32}) A_2 = \Phi_{1,2} h_2. \quad (5.5.11)$$

Here $\delta_{12} = \delta_{\alpha_1\alpha_2} \delta(t_{12})$: U_{32} is a matrix which has the form

$$U_{32} = U_{\alpha_3\alpha_2}(t_3, t_2) = u_{\alpha_3\alpha_2} \delta(t_{32}), \quad (5.5.12)$$

in the time representation. Solving (5.5.11) for A_2 , we have

$$A_2 = (p_1 \delta_{12} + \Phi_{1,3} U_{32})^{-1} \Phi_{1,2} h_2. \quad (5.5.13)$$

Comparison of (5.5.13) with (5.2.4) yields

$$(p_4 \delta_{41} + \Phi_{4,3} U_{31})^{-1} \Phi_{4,2} = G_{1,2}. \quad (5.5.14)$$

Thus, the expression appearing in front of h_2 on the right-hand side of (5.5.13) is nothing but the linear admittance. As we have shown in Sect. 5.3.3, it satisfies the reciprocal relation (5.3.46).

In a more compact notation this relation can be written as $G^{\text{t.c.}} = G^T$. Using equation (5.5.14), which can be written in matrix form

$$(p + \Phi U)^{-1} \Phi = G \quad (G = \|G_{1,2}\|) \quad (5.5.15)$$

(the identity matrix has not been explicitly written, but is implied), we arrive at

$$[(p + \Phi U)^{-1} \Phi]^{\text{t.c.}} = [(p + \Phi U)^{-1} \Phi]^T$$

or

$$(p^{\text{t.c.}} + \Phi^{\text{t.c.}} U^{\text{t.c.}})^{-1} \Phi^{\text{t.c.}} = \Phi^T (p^T + U^T \Phi^T)^{-1}. \quad (5.5.16)$$

But it is easy to see that

$$p^{\text{t.c.}} = -p, \quad p^T = -p, \quad U^T = U, \quad U^{\text{t.c.}} = U. \quad (5.5.17)$$

The formula $U^{\text{t.c.}} = U$, i.e. $\varepsilon_\alpha \varepsilon_\beta u_{\alpha\beta} = u_{\alpha\beta}$, follows from time symmetry of the equilibrium probability density: $w_{\text{eq}}(\varepsilon B) = w_{\text{eq}}(B)$. Equations (5.5.16) are therefore equivalent to

$$(-p + \Phi^{\text{t.c.}} U)^{-1} \Phi^{\text{t.c.}} = \Phi^T (-p + U \Phi^T)^{-1}$$

or

$$\Phi^{\text{t.c.}} (-p + U \Phi^T) = (-p + \Phi^{\text{t.c.}} U) \Phi^T. \quad (5.5.18)$$

Hence we find

$$\Phi^{\text{t.c.}} = \Phi^T. \quad (5.5.19)$$

Equation (5.5.19) or (5.1.25) is the reciprocal relation for the function $\Phi_{1,2}$. This relation has been derived by Markov methods in Sect. 5.1.2.

5.5.3 Linear FDR

Proceeding now to a consideration of fluctuating internal parameters $B_\alpha(t)$, we have, instead of (5.5.9), an equation of the Langevin type

$$\dot{B}_1 = -\Phi_{1,2}(U_{23}B_3 - h_2) + \zeta_1 \quad (5.5.20)$$

(see (5.1.45)).

Our goal is to relate the correlator of the random Langevin forces

$$\Phi_{12} = \langle \zeta_1, \zeta_2 \rangle \quad (5.5.21)$$

to the function $\Phi_{1,2}$. Solving equation (5.5.20) for $h \equiv 0$, i.e. the equation $\dot{B}_1 + \Phi_1 U_1 B_1 = \zeta_1$, where $\Phi = \|\Phi_{1,2}\|$ and $U = \|U_{1,2}\|$, we get

$$B_1 = (p_1 + \Phi_1 U_1)^{-1} \zeta_1. \quad (5.5.22)$$

Equation (5.5.22) gives

$$\langle B_1, B_2 \rangle = (p_1 + \Phi_1 U_1)^{-1} (p_2 + \Phi_2 U_2)^{-1} \langle \zeta, \zeta_2 \rangle. \quad (5.5.23)$$

On the other hand, the correlator of internal parameters $\langle \hat{B}_1, \hat{B}_2 \rangle$ is determined by (5.3.6) in the quantum case. Using (5.5.15), equation (5.3.6) may be written as

$$\langle \hat{B}_1, \hat{B}_2 \rangle = i\hbar \Gamma_2^- [(p_1 - \Phi_1 U_1)^{-1} \Phi_{1,2} - (p_2 - \Phi_2 U_2)^{-1} \Phi_{2,1}]. \quad (5.5.24)$$

We equate the right-hand sides of (5.5.23) and (5.5.24) and let the operators $p_1 + \Phi_1 U_1$ and $p_2 + \Phi_2 U_2$ act on them. Employing the notation of (5.5.21), we arrive at

$$\Phi_{12} = i\hbar \Gamma_2^- [(p_2 - \Phi_2 U_2) \Phi_{1,2} - (p_1 - \Phi_1 U_1) \Phi_{2,1}]. \quad (5.5.25)$$

If $\Phi_2 U_2 \Phi_{1,2}$ and $\Phi_1 U_1 \Phi_{2,1}$ are written out explicitly, we obtain the same expression $\Phi_{1,3} \Phi_{2,4} U_{34}$. Therefore, these expressions can be cancelled; this yields

$$\Phi_{12} = i\hbar \Gamma_2^- (p_2 \Phi_{1,2} - p_1 \Phi_{2,1}) = i\hbar p_2 \Gamma_2^- (\Phi_{1,2} + \Phi_{2,1}). \quad (5.5.26)$$

Hence, using the notation of (5.3.93), we get

$$\Phi_{12} = kT \Theta_2^- (\Phi_{1,2} + \Phi_{2,1}). \quad (5.5.27)$$

Formula (5.5.27) is analogous to (5.3.92). In the nonquantum limit $\hbar \rightarrow 0$, the operators Θ^\pm tend to unity and (5.5.27) goes over into the relation (5.1.53), which was obtained by another method in Sect. 5.1.3.

5.5.4 Linear–Quadratic Approximation: The Connection Between the Function $\Phi_{1,23}$ and the Quadratic Admittance $G_{1,23}$

The equation

$$\dot{A}_\alpha = \Psi_\alpha [x(\cdot) - h(\cdot)], \quad (5.5.28)$$

which follows from (5.5.3, 8), can be written in the form of an expansion

$$\begin{aligned}\dot{A}_1 = & -\Phi_{1,2}(x_2 - h_2) - \frac{1}{2}\Phi_{1,23}(x_2 - h_2)(x_3 - h_3) \\ & - \frac{1}{6}\Phi_{1,234}(x_2 - h_2)(x_3 - h_3)(x_4 - h_4) + \dots\end{aligned}\quad (5.5.29)$$

by analogy with (5.1.4). In the linear-quadratic approximation one can use the equation

$$\dot{A}_1 = -\Phi_{1,2}(x_2 - h_2) - \frac{1}{2}\Phi_{1,23}(x_2 - h_2)(x_3 - h_3), \quad (5.5.30)$$

and instead of (5.5.10) one takes the dependence to be

$$x_\alpha(A) = u_{\alpha\beta} A_\beta + \frac{1}{2}s_{\alpha\beta\gamma} A_\gamma. \quad (5.5.31)$$

If the matrix u is nondegenerate, as assumed here, using a linear transformation of the variables A_α , one can reduce this matrix to the identity matrix, i.e. to $\delta_{\alpha\beta}$. Then instead of (5.5.31) we have

$$x_\alpha = A_\alpha + \frac{1}{2}s_{\alpha\beta\gamma} A_\beta A_\gamma. \quad (5.5.32)$$

We shall use (5.5.32) instead of (5.5.31) for writing the formulas in a somewhat shorter form.

Substituting (5.5.32) into (5.5.30), in the linear-quadratic approximation we have

$$\dot{A}_1 + \Phi_{1,2} A_2 = \Phi_{1,2} h_2 - \frac{1}{2}\Phi_{1,4} S_{423} A_2 A_3 - \frac{1}{2}\Phi_{1,23}(A_2 - h_2)(A_3 - h_3). \quad (5.5.33)$$

Here S_{123} is the matrix:

$$S_{\alpha_1\alpha_2\alpha_3}(t_1, t_2, t_3) = s_{\alpha_1\alpha_2\alpha_3} \delta(t_1 - t_2) \delta(t_1 - t_3). \quad (5.5.34)$$

From (5.5.33) we obtain

$$\begin{aligned}A_1 = & (p_1 + \Phi_1)^{-1} [\Phi_1 h_1 - \frac{1}{2}\Phi_1 S_{123} A_2 A_3 \\ & - \frac{1}{2}\Phi_{1,23}(A_2 - h_2)(A_3 - h_3)].\end{aligned}\quad (5.5.35)$$

Here and subsequently we use the contracted mode of writing formulas, which will be also used in (5.6.11).

If by iterations the whole expression on the right-hand side of (5.5.35) is substituted for A_k into the right-hand side of (5.5.35), then all the A_k on the right-hand side can be expressed in terms of h . One iteration is sufficient in the linear-quadratic approximation. It gives

$$\begin{aligned}A_1 = & T_1 \Phi_1 h_1 - \frac{1}{2} T_1 \Phi_1 S_{123} T_2 \Phi_2 T_3 \Phi_3 h_2 h_3 \\ & - \frac{1}{2} T_1 \Phi_{1,23} (T_2 \Phi_2 - 1) (T_3 \Phi_3 - 1) h_2 h_3 + \dots.\end{aligned}\quad (5.5.36)$$

Here we have used the notation

$$T_1 = (p_1 + \Phi_1)^{-1}. \quad (5.5.37)$$

Comparing (5.5.36) with (5.2.4), we obtain the equation

$$G_{1,2} = T_1 \Phi_{1,2} \quad (5.5.38)$$

(see (5.5.15)) and also

$$G_{1,23} = -T_1 \Phi_{1,23} T_2 \Phi_2 T_3 \Phi_3 - T_1 \Phi_{1,23} (T_2 \Phi_2 - 1) (T_3 \Phi_3 - 1). \quad (5.5.39)$$

Using (5.5.38), we may write (5.5.39) as

$$G_{1,23} = -G_1 S_{123} G_2 G_3 - T_1 \Phi_{1,23} (G_2 - 1) (G_3 - 1). \quad (5.5.40)$$

5.5.5 Stochastic Equation in the Linear–Quadratic Approximation

In the nonlinear approximation, instead of (5.5.20) one considers the equation

$$\begin{aligned} \dot{B}_1 = & -\tilde{\Phi}_{1,2}(x_2 - h_2) - \frac{1}{2}\tilde{\Phi}_{1,23}(x_2 - h_2)(x_3 - h_3) \\ & - \frac{1}{6}\tilde{\Phi}_{1,234}(x_2 - h_2)(x_3 - h_3)(x_4 - h_4) - \dots - M_1 + \sum_{\sigma} [S_{12}^{(\sigma)} \xi_2^{(\sigma)} \\ & + S_{123}^{(\sigma)} \xi_2^{(\sigma)}(x_3 - h_3) + \frac{1}{2}S_{1234}^{(\sigma)} \xi_2^{(\sigma)}(x_3 - h_3)(x_4 - h_4) + \dots]. \end{aligned} \quad (5.5.41)$$

Here $\xi_2^{(1)}, \xi_2^{(2)}, \dots$ are stochastically independent random processes having zero means, their correlators being given by

$$\begin{aligned} \langle \xi_1^{(\sigma)}, \xi_2^{(\sigma)} \rangle &= K_{12}^{(\sigma)}, \\ \langle \xi_1^{(\sigma)}, \xi_2^{(\sigma)}, \xi_3^{(\sigma)} \rangle &= K_{123}^{(\sigma)}, \dots. \end{aligned} \quad (5.5.42)$$

Cross-correlators are equal to zero. The difference between the functions $\tilde{\Phi}_{1,2\dots m}$ in (5.5.41) and the functions $\Phi_{1,2\dots m}$ in (5.1.4) is sufficiently small, namely,

$$\tilde{\Phi}_{1,2\dots m} - \Phi_{1,2\dots m} \sim \kappa. \quad (5.5.43)$$

Here we have $\kappa = kT$ in the nonquantum case and $\kappa = \max(kT, \hbar\omega)$ in the quantum case. For simplicity we shall set $\kappa = kT$. In the linear–quadratic approximation it is not necessary to distinguish between $\tilde{\Phi}_{1,2}, \tilde{\Phi}_{1,23}$ and $\Phi_{1,2}, \Phi_{1,23}$. Omitting terms of higher orders, one can apply the equation

$$\begin{aligned} \dot{B}_1 = & -\Phi_{1,2}(x_2 - h_2) - \frac{1}{2}\Phi_{1,23}(x_2 - h_2)(x_3 - h_3) \\ & + \sum_{\sigma} [S_{12}^{(\sigma)} \xi_2^{(\sigma)} + S_{123}^{(\sigma)} \xi_2^{(\sigma)}(x_3 - h_3)]. \end{aligned} \quad (5.5.44)$$

External forces h appear in (5.5.41, 44) in the same combination $x - h$ in which they appear on the right-hand side of (5.5.30). This means that the hypothesis of the simplest inclusion of forces is also used. If we set

$$F_1[x, \xi] = -\sum_{\sigma} [S_{12} \xi_2^{(\sigma)} + S_{123} \xi_2^{(\sigma)} x_3] \quad (5.5.45)$$

and $h = 0$, then (5.5.44) coincides with (5.1.72).

The functions $\Phi_{12,3}, \Phi_{123}$ are defined by (5.1.73). In our case these functions can be expressed in terms of the functions $S_{12}^{(\sigma)}, S_{123}^{(\sigma)}$ appearing in (5.5.45) and in terms of the correlators (5.5.42). The correlators $\langle F_1, F_2 \rangle_x, \langle F_1, F_2, F_3 \rangle_x$ must be calculated when the argument functions $x_a(t)$ in (5.5.45) are assumed to be fixed. Equations (5.5.42, 45) give

$$\begin{aligned}\langle F_1, F_2 \rangle_x &= \sum_{\sigma} \{ S_1^{(\sigma)} S_2^{(\sigma)} K_{12}^{(\sigma)} + S_{143}^{(\sigma)} S_2^{(\sigma)} K_{42}^{(\sigma)} x_3 + S_1^{(\sigma)} S_{243}^{(\sigma)} K_{14}^{(\sigma)} x_3 \} \\ &= \Phi_{12} + \Phi_{12,3} x_3 ,\end{aligned}\quad (5.5.46a)$$

$$\langle F_1, F_2, F_3 \rangle_{x=0} = - \sum_{\sigma} S_1^{(\sigma)} S_2^{(\sigma)} S_3^{(\sigma)} K_{123}^{(\sigma)} . \quad (5.5.46b)$$

Therefore, we get

$$\Phi_{12} = \sum_{\sigma} S_1^{(\sigma)} S_2^{(\sigma)} K_{12}^{(\sigma)} , \quad (5.5.47)$$

$$\Phi_{12,3} = \sum_{\sigma} (S_{143}^{(\sigma)} S_2^{(\sigma)} K_{42}^{(\sigma)} + S_{243}^{(\sigma)} S_1^{(\sigma)} K_{14}^{(\sigma)}) , \quad (5.5.48)$$

$$\Phi_{123} = - \sum_{\sigma} S_1^{(\sigma)} S_2^{(\sigma)} S_3^{(\sigma)} K_{123}^{(\sigma)} . \quad (5.5.49)$$

Subsequently, in the quantum case we shall use the notations

$$\begin{aligned}\Phi_{12,3}^- &= \sum_{\sigma} S_{143}^{(\sigma)} S_2^{(\sigma)} K_{42}^{(\sigma)}, \\ \Phi_{12,3}^+ &= \sum_{\sigma} S_{143}^{(\sigma)} S_2^{(\sigma)} K_{24}^{(\sigma)} .\end{aligned}\quad (5.5.50)$$

Therefore, by virtue of (5.5.48) we have

$$\Phi_{12,3} = \Phi_{12,3}^- + \Phi_{21,3}^+ . \quad (5.5.51)$$

5.5.6 Derivation of the Quadratic FDR for $\Phi_{12,3}$

Substituting an equation of the type (5.5.32)

$$x_{\alpha} = B_{\alpha} + \frac{1}{2} S_{\alpha\beta\gamma} B_{\beta} B_{\gamma} , \quad (5.5.52)$$

into (5.5.44), in the framework of the linear-quadratic approximation we arrive at

$$\begin{aligned}\dot{B}_1 + \Phi_{1,2} B_2 &= \Phi_{1,2} h_2 - \frac{1}{2} \Phi_{1,4} S_{423} B_2 B_3 - \frac{1}{2} \Phi_{1,23} (B_2 - h_2)(B_3 - h_3) \\ &\quad + \sum_{\sigma} [S_1^{(\sigma)} \xi_1^{(\sigma)} + S_{12,3}^{(\sigma)} \xi_2^{(\sigma)} (B_3 - h_3)] ,\end{aligned}\quad (5.5.53)$$

cf. (5.5.33). Hence we find

$$\begin{aligned}B_1 &= (p_1 + \Phi_1)^{-1} \left\{ \Phi_1 h_1 - \frac{1}{2} \Phi_1 S_{123} B_2 B_3 - \frac{1}{2} \Phi_{1,23} (B_2 - h_2)(B_3 - h_3) \right. \\ &\quad \left. + \sum_{\sigma} [S_1^{(\sigma)} \xi_1^{(\sigma)} + S_{12,3}^{(\sigma)} \xi_2^{(\sigma)} (B_3 - h_3)] \right\} .\end{aligned}\quad (5.5.54)$$

If by iterations we substitute the whole expression on the right-hand side of (5.5.54) for B_k appearing in braces, we can express B_1 in terms of h and $\xi^{(\sigma)}$. Then we can find all possible correlators of the parameters B_l . Now it is sufficient to find the correlator $G_{12} + G_{12,3} h_3$, or more exactly, to find the function $G_{12,3}$ with rather

limited accuracy, namely, by considering only terms of the order of kT . The terms of higher orders in kT may be omitted. Therefore the terms quadratic in h and in $\xi^{(\sigma)}$ and higher-order terms may be neglected in the expression $B_1[h, \xi^{(\sigma)}]$. For calculating $G_{12,3}$ with a given accuracy it is sufficient to use the expression

$$\begin{aligned} B_1 = T_1 & \left\{ -\Phi_1 S_{123} T_2 \sum_{\sigma} S_2^{(\sigma)} \xi_2^{(\sigma)} T_3 \Phi_3 h_3 \right. \\ & - \Phi_{1,23} T_2 \sum_{\sigma} S_2^{(\sigma)} \xi_2^{(\sigma)} (T_3 \Phi_3 - 1) h_3 \\ & \left. + \sum_{\sigma} [S_1^{(\sigma)} \xi_1^{(\sigma)} + S_{123}^{(\sigma)} \xi_2^{(\sigma)} (T_3 \Phi_3 - 1) h_3] \right\}, \end{aligned} \quad (5.5.55)$$

which is obtained from (5.5.54). Here the notation (5.5.37) is used. In (5.5.55) we have taken into account the fact that the terms containing no random functions have no influence on the correlator $\langle B_1, B_2 \rangle$.

Using (5.5.55) for calculating the correlator $\langle B_1, B_2 \rangle$ with the necessary accuracy, we obtain in the quantum case

$$\begin{aligned} G_{12,3} = & -T_1 T_2 \sum_{\sigma} [(\Phi_1 S_{143} T_4 K_{42}^{(\sigma)} + \Phi_2 S_{243} T_4 K_{14}^{(\sigma)}) T_3 \Phi_3 \\ & + (\Phi_{1,43} T_4 K_{42}^{(\sigma)} + \Phi_{2,43} T_4 K_{14}^{(\sigma)}) (T_3 \Phi_3 - 1) \\ & - (S_{14,3}^{(\sigma)} K_{42}^{(\sigma)} + S_{24,3}^{(\sigma)} K_{14}^{(\sigma)}) (T_3 \Phi_3 - 1)]. \end{aligned} \quad (5.5.56)$$

Here and subsequently $S_{12}^{(\sigma)}$ are assumed to be equal to the identity matrix in order to simplify the notation.

By using (5.5.38, 49) and the linear-theory formula $G_{12} = T_1 T_2 \Phi_{12} = T_1 T_2 \Sigma_{\sigma} K_{12}^{(\sigma)}$ [see (5.5.48)], which is analogous to (5.5.23), equation (5.5.56) can be written in the form

$$\begin{aligned} G_{12,3} = & -(G_1 S_{143} G_{42} + G_2 S_{243} G_{14}) G_3 \\ & - (T_1 \Phi_{1,43} G_{42} + T_2 \Phi_{2,43} G_{14}) (G_3 - 1) + T_1 T_2 \Phi_{12,3} (G_3 - 1). \end{aligned} \quad (5.5.57)$$

Using (5.3.6), we can express G_{jk} in terms of $G_{m,n}$ and from (5.5.57) we obtain

$$\begin{aligned} G_{12,3} = & -i\hbar [\Gamma_2^- G_1 S_{123} (G_2 - G_2^T) + \Gamma_1^+ G_2 S_{213} (G_1 - G_1^T)] G_3 \\ & - i\hbar [\Gamma_2^- T_1 \Phi_{1,23} (G_2 - G_2^T) + \Gamma_1^+ T_2 \Phi_{2,13} (G_1 - G_1^T)] (G_3 - 1) \\ & + T_1 T_2 \Phi_{12,3} (G_3 - 1). \end{aligned} \quad (5.5.58)$$

On the other hand, the biadmittance $G_{12,3}$ is determined by (5.3.89). Substitution of (5.5.40) into (5.3.89) yields

$$\begin{aligned} G_{12,3} = & i\hbar \{ -\Gamma_2^- [G_1 S_{123} G_2 G_3 + T_1 \Phi_{1,23} (G_2 - 1)(G_3 - 1)] \\ & - \Gamma_1^+ [G_2 S_{213} G_1 G_3 + T_2 \Phi_{2,13} (G_1 - 1)(G_3 - 1)] \\ & + (\Gamma_1^+ + \Gamma_2^-) [G_1 G_2 S_{312} G_3 + (G_1 - 1)(G_2 - 1) \Phi_{3,12}^{t,c} T_3] \}. \end{aligned} \quad (5.5.59)$$

Here we have used the relation $S_{312}^{t,c} = S_{312}$ based on the equation $\epsilon_{\alpha} \epsilon_{\beta} \epsilon_{\gamma} s_{\alpha\beta\gamma} = s_{\alpha\beta\gamma}$,

which in turn follows from the invariance of the equilibrium probability density under time reversal: $w_{\text{eq}}(\varepsilon B) = w_{\text{eq}}(B)$. We have also used the equation $[(p_3 + \Phi_3)^{-1}]^{\text{t.c.}} = [(p_3 + \Phi_3)^{-1}]^T$, i.e. $T^{\text{t.c.}} = T^T$, which follows from (5.5.19).

Equating (5.5.58) and (5.5.59), we see that a number of terms cancel out; in particular, all terms with S_{klm} drop out as a consequence of the symmetry of the type $S_{klm} = S_{lkm}$. Thus we have

$$\begin{aligned} & [T_1 T_2 \Phi_{12,3} + i\hbar \Gamma_2^- (G_2 - 1) T_1 \Phi_{1,23} + i\hbar \Gamma_1^+ (G_1 - 1) T_2 \Phi_{2,13}] (G_3 - 1) \\ & = i\hbar (\Gamma_1^+ + \Gamma_2^-) (G_1 - 1) (G_2 - 1) \Phi_{3,12}^{\text{t.c.}} T_3 . \end{aligned} \quad (5.5.60)$$

Using (5.5.37, 38), we easily prove that $G_l - 1 = -p_l T_l$. Substituting this equation into (5.5.60) and cancelling T_1, T_2, T_3 , we finally arrive at

$$\Phi_{12,3} = kT [\Theta_2^- \Phi_{1,23} + \Theta_1^+ \Phi_{2,13} + (p_1 \Theta_2^- + p_2 \Theta_1^+) p_3^{-1} \Phi_{3,12}^{\text{t.c.}}] . \quad (5.5.61)$$

Here we have also used the relation $\Phi_{3,12}^{\text{t.c.}} p_3^{-1} = -p_3^{-1} \Phi_{3,12}^{\text{t.c.}}$. The structure of (5.5.61) is analogous to the structure of (5.3.97). The quadratic FDR of the first kind (5.5.61) implies (5.1.74) in the nonquantum limit $\hbar \rightarrow 0$.

5.5.7 Another Quadratic FDR

In order to derive the relation for the function Φ_{123} , one has to find the equilibrium correlator $\langle B_1, B_2, B_3 \rangle_0 = G_{123}$ corresponding to vanishing external forces. In doing so, one should set $h = 0$ in (5.5.54) and express B_k appearing on the right-hand side in terms of $\xi^{(\sigma)}$, retaining only the terms linear and quadratic in $\xi^{(\sigma)}$. One can use the expression

$$\begin{aligned} B_1 = T_1 \left\{ & -\frac{1}{2} (\Phi_1 S_{123} + \Phi_{1,23}) T_2 T_3 \sum_{\tau, \rho} \xi_2^{(\tau)} \xi_3^{(\rho)} \right. \\ & \left. + \sum_{\sigma} \left[\xi_1^{(\sigma)} + \sum_{\tau} S_{12,3}^{(\sigma)} \xi_2^{(\sigma)} T_3 \xi_3^{(\tau)} \right] \right\} \end{aligned} \quad (5.5.62)$$

obtained from (5.5.54).

To calculate $\langle B_1, B_2, B_3 \rangle_0$ one need take into account only terms of the order of $(kT)^2$. These are the terms which are linear in $K_{123}^{(\sigma)}$ and quadratic in $K_{12}^{(\sigma)}$. Using the rule that has been discussed in connection with (2.1.15, 16) in Sect. 2.1.2 for calculating the correlator, we arrive at

$$\begin{aligned} G_{123} = T_1 T_2 T_3 \left\{ & \sum_{\sigma} K_{123}^{(\sigma)} + \sum_{\sigma, \tau} [S_{145}^{(\sigma)} T_5 (K_{42}^{(\sigma)} K_{53}^{(\tau)} + K_{43}^{(\sigma)} K_{52}^{(\tau)}) \right. \\ & + S_{24,5}^{(\sigma)} T_5 (K_{14}^{(\sigma)} K_{53}^{(\tau)} + K_{43}^{(\sigma)} K_{15}^{(\tau)}) + S_{34,5}^{(\sigma)} T_5 (K_{14}^{(\sigma)} K_{25}^{(\tau)} \\ & + K_{24}^{(\sigma)} K_{15}^{(\tau)})] - (\Phi_1 S_{145} + \Phi_{1,45}) T_4 T_5 \sum_{\sigma \tau} K_{42}^{(\sigma)} K_{53}^{(\tau)} \\ & - (\Phi_2 S_{245} + \Phi_{2,45}) T_4 T_5 \sum_{\sigma \tau} K_{14}^{(\sigma)} K_{53}^{(\tau)} \\ & \left. - (\Phi_3 S_{345} + \Phi_{3,45}) T_4 T_5 \sum_{\sigma \tau} K_{14}^{(\sigma)} K_{25}^{(\tau)} \right\} . \end{aligned} \quad (5.5.63)$$

Using (5.5.49, 50), (5.5.38) and equation $T_1 T_2 \Sigma_\sigma K_{12}^{(\sigma)} = G_{12}$, we find from (5.5.63)

$$\begin{aligned} G_{123} = & -T_1 T_2 T_3 \Phi_{123} + T_1 T_2 \Phi_{12,5} G_{53} + T_1 T_3 (\Phi_{13,5}^- G_{52} + \Phi_{31,5}^+ G_{25}) \\ & + T_2 T_3 \Phi_{23,5} G_{15} - (G_1 S_{145} + T_1 \Phi_{1,45}) G_{42} G_{53} \\ & - (G_2 S_{245} + T_2 \Phi_{2,45}) G_{14} G_{53} - (G_3 S_{345} + T_3 \Phi_{3,45}) G_{14} G_{25}. \end{aligned} \quad (5.5.64)$$

Substitution of (5.3.6) into (5.5.64) gives

$$\begin{aligned} G_{123} = & -T_1 T_2 T_3 \Phi_{123} + i\hbar [T_1 T_2 \Gamma_3^- \Phi_{12,3} (G_3 - G_3^\text{T}) \\ & + T_1 T_3 (\Gamma_2^- \Phi_{13,2}^- + \Gamma_2^+ \Phi_{31,2}^+) (G_2 - G_2^\text{T}) + T_2 T_3 \Gamma_1^+ \Phi_{23,1} (G_1 - G_1^\text{T})] \\ & + \hbar^2 [\Gamma_2^- \Gamma_3^- (G_1 S_{123} + T_1 \Phi_{1,23}) (G_2 - G_2^\text{T}) (G_3 - G_3^\text{T}) \\ & + \Gamma_1^+ \Gamma_3^- (G_2 S_{213} + T_2 \Phi_{2,13}) (G_1 - G_1^\text{T}) (G_3 - G_3^\text{T}) \\ & + \Gamma_1^+ \Gamma_2^+ (G_3 S_{312} + T_3 \Phi_{3,12}) (G_1 - G_1^\text{T}) (G_2 - G_2^\text{T})]. \end{aligned} \quad (5.5.65)$$

Alternatively, G_{123} may be determined by relation (5.3.65), which, as a consequence of (5.5.40), takes the form

$$\begin{aligned} G_{123} = & \hbar^2 [\Gamma_2^- \Gamma_3^- [G_1 S_{123} G_2 G_3 + G_2 G_3 S_{123} G_1 \\ & + T_1 \Phi_{1,23} (G_2 - 1) (G_3 - 1) + (G_2 - 1) (G_3 - 1) \Phi_{1,23}^{\text{t.c.}} T_1] \\ & + \Gamma_1^+ \Gamma_3^- [G_2 S_{231} G_3 G_1 + G_3 G_1 S_{231} G_2 + T_2 \Phi_{2,13} (G_1 - 1) (G_3 - 1) \\ & + (G_1 - 1) (G_3 - 1) \Phi_{2,13}^{\text{t.c.}} T_2] + \Gamma_1^+ \Gamma_2^+ [G_3 S_{312} G_1 G_2 + G_1 G_2 S_{312} G_3 \\ & + T_3 \Phi_{3,12} (G_1 - 1) (G_2 - 1) + (G_1 - 1) (G_2 - 1) \Phi_{3,12}^{\text{t.c.}} T_3]\}. \end{aligned} \quad (5.5.66)$$

Let us substitute (5.5.61) into (5.5.65) and equate (5.5.65) to (5.5.66). Then, as can be easily verified, the matrices S_{klm} cancel out by virtue of (5.2.104). Transposing G_1, G_2, G_3 to the left of the three-subscript functions and using the equations

$$G_l - 1 = -p_l T_l, \quad G_l^\text{T} - 1 = p_l T_l^\text{T}, \quad G_l^\text{T} - G_l = p_l (T_l^\text{T} + T_l) \quad (5.5.67)$$

and also the identity (5.2.104), after cancellations we arrive at

$$\begin{aligned} -\beta^2 \Phi_{123} = & -\Theta_1^+ \Theta_3^- \Phi_{2,13} + \Theta_1^+ \Theta_2^+ \Phi_{3,12}^{\text{t.c.}} + \Theta_2^- \Theta_3^- \Phi_{1,23}^{\text{t.c.}} \\ & - \Theta_2^- \beta \Phi_{13,2}^- - \Theta_2^+ \beta \Phi_{31,2}^+ \end{aligned} \quad (5.5.68)$$

if we set

$$\Theta_2^- \beta \Phi_{13,2}^- + \Theta_2^+ \beta \Phi_{31,2}^+ - \Theta_2^- \Theta_3^- \Phi_{1,23} - \Theta_1^+ \Theta_2^+ \Phi_{3,12} = -\Theta_1^+ \Theta_3^- \Phi_{2,13}^{\text{t.c.}}. \quad (5.5.69)$$

By virtue of (5.2.104) the right-hand side of (5.5.69) may be written as follows: $(p_3 \Theta_1^+ \Theta_2^+ + p_1 \Theta_2^- \Theta_3^-) p_2^{-1} \Phi_{2,13}^{\text{t.c.}}$. In the nonquantum case when $\Theta_k^\pm = 1$, equation (5.5.69) is valid on account of (5.5.51, 61). In the quantum case equation (5.5.69) is a necessary and sufficient condition for the absence of the strange combination $T_{13}^{-1} T_{23}$ in the expression for Φ_{123} obtained from (5.5.65, 66). Defining

$$\begin{aligned} X &= \beta \Phi_{13,2}^- - \Theta_3^- \Phi_{1,23} - p_1 \Theta_3^- p_2^{-1} \Phi_{2,13}^{\text{t.c.}}, \\ Y &= \beta \Phi_{31,2}^+ - \Theta_1^+ \Phi_{3,12} - p_3 \Theta_1^+ p_2^{-1} \Phi_{2,13}^{\text{t.c.}}, \end{aligned} \quad (5.5.70)$$

equation (5.5.69) can be written as $\Theta_2^- X + \Theta_2^- Y = 0$, while (5.5.61) (with interchanged subscripts 2 and 3) can be written as $X + Y = 0$. These two equations can be regarded as a system of equations from which one can find X and Y . This system is nondegenerate in the quantum case; we obtain from it $X = 0$, $Y = 0$, or by virtue of (5.5.70)

$$\beta\Phi_{13,2}^\pm = \Theta_3^\pm(\Phi_{1,23} + p_1 p_2^{-1} \Phi_{2,13}^{\text{t.c.}}). \quad (5.5.71)$$

According to (5.5.69), equation (5.5.68) is reduced to the form

$$\begin{aligned} \beta^2 \Phi_{123} = & \Theta_2^- \Theta_3^- (\Phi_{1,23} - \Phi_{1,23}^{\text{t.c.}}) + \Theta_1^+ \Theta_3^- (\Phi_{2,13} - \Phi_{2,13}^{\text{t.c.}}) \\ & + \Theta_1^+ \Theta_2^+ (\Phi_{3,12} - \Phi_{3,12}^{\text{t.c.}}). \end{aligned} \quad (5.5.72)$$

This is the second quadratic FDR of the first kind. Its structure is similar to the structure of (5.3.95). In the nonquantum limit, (5.5.72) transforms to (5.1.90). We emphasize that an additional postulation of the validity of (5.5.69) is not necessary for deriving the nonquantum FDR (5.1.90) from (5.5.65, 66).

5.5.8 Necessary Conditions Imposed on the Method of External Force Inclusion in the Markov Case: Linear–Quadratic Approximation

In the Markov (nonquantum) case, FDRs (5.5.27, 61, 72) give the Markov FDRs (4.1.12, 16, 18) since in this case

$$\begin{aligned} \Phi_{1,2} &= -l_{\alpha_1, \alpha_2}\delta(t_{12}), \quad \Phi_{12} = l_{\alpha_1 \alpha_2}\delta(t_{12}), \\ \Phi_{1,23} &= -l_{\alpha_1, \alpha_2 \alpha_3}\delta(t_1, t_2, t_3), \quad \Phi_{12,3} = l_{\alpha_1 \alpha_2, \alpha_3}\delta(t_1, t_2, t_3), \\ \Phi_{123} &= -l_{\alpha_1 \alpha_2 \alpha_3}\delta(t_1, t_2, t_3). \end{aligned} \quad (5.5.73)$$

From the considerations of the preceding sections it follows that the rule of the simplest inclusion of external forces is a sufficient condition for consistency of the Markov FDRs and the general FDRs of the second kind. This section will consider the necessary conditions for this consistency in the linear–quadratic approximation.

In the Markov case, (5.5.3) becomes inertialess and takes the form

$$\dot{A}_\alpha = -\Omega_\alpha(x(A), h). \quad (5.5.74)$$

Here the functions Ω_α depend only on $x(A(t))$, $h(t)$ taken at the same moment as $\dot{A}(t)$. Condition (5.5.7) assumes the form

$$\Omega_\alpha(x, h) = 0, \quad \text{for } x = h. \quad (5.5.75)$$

In the linear case this yields

$$\frac{\partial \Omega_\alpha}{\partial x_\beta} + \frac{\partial \Omega_\alpha}{\partial h_\beta} = 0 \quad \text{for } x = 0, h = 0. \quad (5.5.76)$$

For deriving (5.5.76) it is necessary to expand the functions $\Omega_\alpha(x, h)$ in Taylor series about the zero point, insert the expansion into (5.5.75), retain only linear terms and use the arbitrariness of vector h .

Considering also the quadratic terms in the expansion, from (5.5.75) we have

$$\frac{\partial^2 \Omega_\alpha}{\partial x_\beta \partial x_\gamma} + \frac{\partial^2 \Omega_\alpha}{\partial x_\beta \partial h_\gamma} + \frac{\partial^2 \Omega_\alpha}{\partial h_\beta \partial x_\gamma} + \frac{\partial^2 \Omega_\alpha}{\partial h_\beta \partial h_\gamma} = 0 \quad \text{for } x = h = 0. \quad (5.5.77)$$

As a consequence of (5.5.76), in the linear approximation we obtain

$$\Omega_\alpha(x, h) = (\partial \Omega_\alpha / \partial x_\beta)_0 (x_\beta - h_\beta). \quad (5.5.78)$$

This means that in the linear approximation the rule of the simplest inclusion of external forces is confirmed.

Proceeding to the quadratic case, we see that (5.5.77) allows us to independently prescribe, besides $(\partial^2 \Omega_\alpha / \partial x_\beta \partial x_\gamma)_0$, the matrix $(\partial^2 \Omega_\alpha / \partial x_\beta \partial h_\gamma)_0$. Then the matrix $(\partial^2 \Omega_\alpha / \partial h_\beta \partial h_\gamma)$ will be unambiguously determined. Defining

$$m_{\alpha\beta\gamma} = \left(\frac{\partial^2 \Omega_\alpha}{\partial x_\beta \partial h_\gamma} \right)_0 + \left(\frac{\partial^2 \Omega_\alpha}{\partial x_\beta \partial x_\gamma} \right)_0, \quad (5.5.79)$$

from (5.5.77) we have

$$\left(\frac{\partial^2 \Omega_\alpha}{\partial h_\beta \partial h_\gamma} \right)_0 = \left(\frac{\partial^2 \Omega_\alpha}{\partial x_\beta \partial x_\gamma} \right)_0 - m_{\alpha\beta\gamma} - m_{\alpha\gamma\beta}. \quad (5.5.80)$$

The function

$$\begin{aligned} \Omega_\alpha(x, h) = & \left(\frac{\partial \Omega_\alpha}{\partial x_\beta} \right)_0 (x_\beta - h_\beta) + \frac{1}{2} \left(\frac{\partial^2 \Omega_\alpha}{\partial x_\beta \partial x_\gamma} \right)_0 (x_\beta - h_\beta)(x_\gamma - h_\gamma) \\ & + m_{\alpha\beta\gamma}(x_\beta - h_\beta)h_\gamma. \end{aligned} \quad (5.5.81)$$

corresponds to (5.5.80). We see from (5.5.81) that the nonzero values of elements of the matrix $m_{\alpha\beta\gamma}$ mean a deviation from the rule of the simplest inclusion of external forces in the linear–quadratic approximation. It will be shown later that the condition for consistency of the Markov FDRs and the general FDRs of the second kind leads to an additional equation

$$m_{\alpha\beta\gamma} = \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma m_{\beta\alpha\gamma} \quad (5.5.82)$$

or, by virtue of (5.5.79), to the equation

$$\left(\frac{\partial^2 \Omega_\alpha}{\partial x_\beta \partial h_\gamma} \right)_0 + \left(\frac{\partial^2 \Omega_\alpha}{\partial x_\beta \partial x_\gamma} \right)_0 = \varepsilon_\alpha \varepsilon_\beta \varepsilon_\gamma \left[\left(\frac{\partial^2 \Omega_\beta}{\partial x_\alpha \partial h_\gamma} \right)_0 + \left(\frac{\partial^2 \Omega_\beta}{\partial x_\alpha \partial x_\gamma} \right)_0 \right]. \quad (5.5.83)$$

The latter and (5.5.76, 77) constitute the necessary conditions imposed on the method of inclusion of external forces.

We now proceed to the proof of (5.5.82). In formulas (5.5.30, 33, 35) an additional term must appear due to the term containing $m_{\alpha\beta\gamma}$ in (5.5.81). Thus, instead of (5.5.35) we arrive at

$$A_1 = (p_1 + \Phi_1)^{-1} [\dots + m_{123}(A_2 - h_2)h_3], \quad (5.5.84)$$

where the notation $m_{123} = m_{\alpha_1\alpha_2\alpha_3} \delta(t_1, t_2, t_3)$ has been introduced. In equation

(5.5.84) the terms not written out explicitly (denoted by dots) are those already appearing in (5.5.35). Further, on the right-hand side of (5.5.36) the additional term $T_1 m_{123} (T_2 \Phi_2 - 1) h_2 h_3$ appears, so that instead of (5.5.40) we obtain

$$\begin{aligned} G_{1,23} &= \dots + T_1 [m_{123}(G_2 - 1) + m_{132}(G_3 - 1)] \\ &= \dots + T_1 (p_2 m_{123} T_2 + p_3 m_{132} T_3) . \end{aligned} \quad (5.5.85)$$

As before, here and subsequently, the terms that have already appeared are denoted by dots.

Substituting (5.5.85) into (5.3.72), instead of equation (5.5.66) taken in the nonquantum variant, we arrive at

$$G_{123} = \dots + (kT)^2 P_{123} (p_3^{-1} T_1 m_{123} T_2 - \varepsilon_1 \varepsilon_2 \varepsilon_3 p_3^{-1} T_2 m_{123} T_1) \quad (5.5.86)$$

or

$$G_{123} = \dots + (kT)^2 P_{123} p_3^{-1} T_1 (m_{123} - \varepsilon_1 \varepsilon_2 \varepsilon_3 m_{213}) T_2 \quad (5.5.87)$$

if we rearrange the terms. Correction terms that contain m_{ikl} must be equal to zero since the correlator G_{123} is quite unambiguously determined by the Markov FDRs which coincide with the nonquantum variant of (5.5.27, 61, 72). Consequently, the expression appearing in (5.5.87) after the dots must be equal to zero. If we write it in the spectral representation and use (5.5.37), we obtain

$$P_{123} \omega_3^{-1} (i\omega_1 \hat{I}_1 + \hat{D}_1)^{-1} (-i\omega_2 \hat{I}_2 + \hat{D}_2)^{-1} (m_{\alpha_1 \alpha_2 \alpha_3} - \varepsilon_{\alpha_1} \varepsilon_{\alpha_2} \varepsilon_{\alpha_3} m_{\alpha_2 \alpha_1 \alpha_3}) = 0 . \quad (5.5.88)$$

This equation must be valid for any $\omega_1, \omega_2, \omega_3$. Here $\hat{D} = -\|l_{\alpha, \beta}\|$ or $\hat{D} = -\|l_{\alpha, \gamma} u_{\gamma \beta}\| \equiv \|d_{\alpha \beta}\|$ if $u_{\gamma \beta}$ is not equal to the identity matrix. In order that (5.5.88) be valid for $\omega_3 \rightarrow 0$, the following equation must hold:

$$P_{12} (i\omega_1 \hat{I}_1 + \hat{D}_1)^{-1} (-i\omega_2 \hat{I}_2 + \hat{D}_2)^{-1} (m_{\alpha_1 \alpha_2 \alpha_3} - \varepsilon_{\alpha_1} \varepsilon_{\alpha_2} \varepsilon_{\alpha_3} m_{\alpha_2 \alpha_1 \alpha_3}) = 0 . \quad (5.5.89)$$

Premultiplying (5.5.89) by $-i\omega_1 \hat{I}_1 + \hat{D}_1$ and $-i\omega_2 \hat{I}_2 + \hat{D}_2$ and twice differentiating the result with respect to ω_1 or ω_2 , we obtain (5.5.82).

It follows from (5.5.82) that for one time-odd parameter B_α , the matrix m is equal to zero and the rule of the simplest inclusion of external forces is valid. In the many-component case a number of elements of the matrix m must be equal to zero if time-odd parameters are present. The other elements are not necessarily equal to zero. However, this does not exclude the possibility that in many cases $m_{\alpha \beta \gamma} = 0$ for all α, β, γ .

Note that, equating expressions of the types (5.5.58, 59), we are unable to give new relations for $m_{\alpha \beta \gamma}$ since terms of the form $\sum_\sigma R_{12,3}^{(\sigma)} \xi_2^{(\sigma)} h_3$ may be added to the stochastic representation (5.5.54) if we do not accept the hypothesis of the simplest inclusion of external forces. Then, if we equate expressions of the types (5.5.58, 59), we learn only how the sum $\sum_\sigma (R_{14,3}^{(\sigma)} K_{43}^{(\sigma)} + R_{24,3}^{(\sigma)} K_{14}^{(\sigma)})$ is expressed by $m_{\alpha \beta \gamma}$.

The conditions (5.5.77, 83) were obtained in [5.9].

5.6 Linear and Quadratic FDRs of the Third Kind

5.6.1 Definition of Impedances

Fluctuations of internal thermodynamic parameters $B_\alpha(t)$ and of the corresponding fluxes $J_\alpha = \dot{B}_\alpha$ can be explained by the fact that the random forces that are the thermodynamic conjugates of B_α arise in different dissipative elements of the physical system under study. The statistical characteristics of random forces and impedances of the system are connected by universal relations, which are called FDRs of the third kind.

Proceeding to the definition of impedances, we use (5.2.4), which shows how average parameters $A_\alpha = \langle B_\alpha \rangle$ are expressed in terms of external forces h_α . The inverse dependence can be written as

$$h_1 = Q_{1,2}A_2 + \frac{1}{2}Q_{1,23}A_2A_3 + \frac{1}{6}Q_{1,234}A_2A_3A_4 + \dots \quad (5.6.1)$$

Equation (5.6.1) is the definition of impedances $Q_{1,2\dots m}$. In order to find how impedances are expressed in terms of admittances (5.2.3), one should solve (5.2.4) for h_1 by iteration. From (5.2.4) we have

$$G_{2,3}h_3 = A_2 - \frac{1}{2}G_{2,34}h_3h_4 - \frac{1}{6}G_{2,345}h_3h_4h_5 - \dots \quad (5.6.2)$$

We introduce the matrix $Q_{1,2}$, which is the inverse of $G_{1,2}$ (we assume that $G_{1,2}^{-1}$ exists). This means that the equation $Q_{1,2}G_{2,3}h_3 = h_1$ must be valid. Letting the operator $Q_{1,2}$ act on both sides of (5.6.2), we have

$$h_1 = Q_{1,2}A_2 - \frac{1}{2}Q_{1,2}G_{2,34}h_3h_4 - \frac{1}{6}Q_{1,2}G_{2,345}h_3h_4h_5 - \dots \quad (5.6.3)$$

Let us substitute an expression of the type (5.6.3), namely,

$$h_3 = Q_{3,6}A_6 - \frac{1}{2}Q_{3,6}G_{6,78}h_7h_8 - \dots \quad (5.6.4)$$

for h_3, h_4, \dots into the right-hand side of (5.6.3). This yields

$$\begin{aligned} h_1 &= Q_{1,2}A_2 - \frac{1}{2}Q_{1,2}G_{2,34}Q_{3,5}Q_{4,6}A_5A_6 \\ &\quad - \frac{1}{6}Q_{1,2}G_{2,345}Q_{3,6}Q_{4,7}Q_{5,8}A_6A_7A_8 \\ &\quad + \frac{1}{4}Q_{1,2}G_{2,34}[Q_{3,5}Q_{4,6} + Q_{3,6}Q_{4,5}]A_5G_{6,78}h_7h_8 - \dots \end{aligned} \quad (5.6.5)$$

Continuing to make substitutions of this type and comparing the resultant expansion with (5.6.1), we can find impedances to any order. In particular, for impedances written in (5.6.1) we obtain

$$Q_{1,2} = G_{1,2}^{-1}, \quad (5.6.6a)$$

$$Q_{1,23} = -Q_{1,4}G_{4,56}Q_{5,2}Q_{6,3}, \quad (5.6.6b)$$

$$\begin{aligned} Q_{1,234} &= Q_{1,5}[-G_{5,678} + G_{5,69}Q_{9,l}G_{l,78} \\ &\quad + G_{5,79}Q_{9l}G_{l,68} + G_{5,89}Q_{9,l}G_{l,67}]Q_{6,2}Q_{7,3}Q_{8,4}. \end{aligned} \quad (5.6.6c)$$

As we see from (5.6.1, 6), impedances are symmetric in the subscripts appearing

after the comma, i.e. they satisfy equations of the type (5.2.5). Like admittances, impedances satisfy the causality condition

$$\eta_{21} Q_{1,2 \dots m} = 0 . \quad (5.6.7)$$

It is easy to see that the causality condition for impedances (5.6.7) follows from the corresponding causality condition for admittances $G_{1,2}$, $G_{1,23}$, $G_{1,234}$.

If we differentiate (5.2.4) (taken in the time representation) with respect to t_1 , we obtain (5.2.8), where modified admittances $Y_{1,2 \dots m}$ are determined by (5.2.7). Writing the inverse dependence of (5.2.8), we get the equation

$$h_1 = Z_{1,2} J_2 + \frac{1}{2} Z_{1,23} J_2 J_3 + \frac{1}{6} Z_{1,234} J_2 J_3 J_4 + \dots , \quad (5.6.8)$$

which is used to define modified impedances $Z_{1,2 \dots m}$. Substituting $J_l = p_l A_l$ into the right-hand side of (5.6.8), we can find a relation between $Q_{1,2 \dots m}$ and $Z_{1,2 \dots m}$. Comparison of the resultant equation with (5.6.1) yields

$$Q_{1,2 \dots m} = Z_{1,2 \dots m} p_2 \dots p_m \quad (5.6.9)$$

or

$$Q_{1,2 \dots m} = p_2^T \dots p_m^T Z_{1,2 \dots m} = (-)^{m-1} p_2 \dots p_m Z_{1,2 \dots m} \quad (5.6.10)$$

since the operation of transposition, which is denoted by superscript T, transforms the operator p into $-p$.

Let us agree to employ the matrix or operator notations to two-subscript matrices $Q_{1,2}$, $Z_{1,2}$, $G_{1,2}$, $Y_{1,2}$ in order to shorten the notation, in analogy with (5.6.9, 10). Namely, we shall write $Q_1 G_{156}$ or $G_{156} Q_1^T$ instead of $Q_{1,4} G_{456}$, and $G_{426} Q_2$ or $Q_2^T G_{426}$ instead of $G_{456} Q_{5,2}$. Using this notation, (5.6.6b, c) become

$$\begin{aligned} Q_{1,23} &= -Q_1 G_{1,23} Q_2 Q_3 = -Q_1 Q_2^T Q_3^T G_{1,23} , \\ Q_{1,234} &= Q_1 Q_2^T Q_3^T Q_4^T [-G_{1,234} + P_{(234)} G_{1,25} Q_5 G_{5,34}] , \end{aligned} \quad (5.6.11)$$

where $P_{(234)}$ denotes the sum over cyclic permutations of subscripts 2, 3, 4.

In conclusion of this section we note that to find $Q_{1,2}$ it is convenient to perform the inversion of the matrix $G_{1,2}$ in the spectral representation. In this representation $G_{1,2}$ is of the form: $G_{\alpha,\beta}(\omega_1, \omega_2) = G'_{\alpha,\beta}(\omega_1) \delta(\omega_1 + \omega_2)$ according to (5.2.21). Therefore

$$G_{1,2} h_2 = \int G_{\alpha_1,\beta}(\omega_1, \omega_2) h_\beta(\omega_2) d\omega_2 = G'_{\alpha_1,\beta}(\omega_1) h_\beta(-\omega_1) . \quad (5.6.12)$$

Substitution of (5.6.12) into formula $Q_{1,3} G_{3,2} h_2 = h_1$ gives

$$\int Q_{\alpha_1,\gamma}(\omega_1, \omega_3) G'_{\gamma,\beta}(\omega_3) h_\beta(-\omega_3) d\omega_3 = h_{\alpha_1}(\omega_1) . \quad (5.6.13)$$

It is easy to see that (5.6.13) holds if

$$Q_{\alpha,\gamma}(\omega_1, \omega_3) = [G'_{\gamma,\alpha}(-\omega_1)]^{-1} \delta(\omega_1 + \omega_3) . \quad (5.6.14)$$

Comparing (5.6.14) with (5.2.29), i.e. according to the notation of this section with equation $Q_{1,2} = Q'_{\alpha_1,\alpha_2}(-\omega_1) \delta(\omega_1 + \omega_2)$, we obtain

$$\| Q'_{\alpha,\gamma}(\omega) \| = \| G'_{\gamma,\alpha}(\omega) \|^{-1} . \quad (5.6.15)$$

Here the “small” matrices obtained by varying subscripts α, β for a fixed value of ω are implied. The “large” matrices obtained by varying $\alpha_1, t_1, \alpha_2, t_2$ or $\alpha_1, \omega_1, \alpha_2, \omega_2$ enter into (5.6.6a).

5.6.2 Reciprocal Relations for Linear Impedance

The fact that the admittance $G_{1,2}$ satisfies the reciprocal relation (5.3.46) or (5.3.47) implies a reciprocal relation for the impedance $Q_{1,2}$ as well.

We first suppose that all parameters B_α are time-even, i.e. all $\varepsilon_\alpha = 1$. Then (5.3.47) means that the matrix $G'_{\alpha,\beta}(\omega)$ is symmetric. But a symmetric matrix has a symmetric inverse. Consequently, matrix (5.6.15) is symmetric, i.e.

$$Q'_{\beta,\alpha}(\omega) = Q'_{\alpha,\beta}(\omega). \quad (5.6.16)$$

Thus, reciprocal relations hold in this particular case. The same result is also valid when all parameters are time-odd.

We now proceed to the general case when we have both time-even and time-odd parameters. We order them as follows: $B = (C, D)$, where C is the set of time-even parameters and D the set of time-odd ones. Then the matrix $G'_{\alpha,\beta}(\omega)$ can be written in block form:

$$\| G'_{\alpha,\beta}(\omega) \| = \begin{pmatrix} R(\omega) & U(\omega) \\ V(\omega) & S(\omega) \end{pmatrix}. \quad (5.6.17)$$

Here $R(\omega)$ corresponds to the time-even parameters and $S(\omega)$ to the time-odd ones; $U(\omega)$ and $V(\omega)$ are cross-matrices, which are not square in the general case. The transposition of matrix (5.6.17) yields

$$\begin{pmatrix} R^T(\omega) & V^T(\omega) \\ U^T(\omega) & S^T(\omega) \end{pmatrix}. \quad (5.6.18)$$

Using the signatures $\varepsilon_\alpha \varepsilon_\beta$ appearing in (5.3.47), we write it in the form

$$\begin{pmatrix} R^T(\omega) & -V^T(\omega) \\ -U^T(\omega) & S^T(\omega) \end{pmatrix} = \begin{pmatrix} R(\omega) & U(\omega) \\ V(\omega) & S(\omega) \end{pmatrix}, \quad (5.6.19)$$

i.e.

$$R^T(\omega) = R(\omega), \quad (5.6.20a)$$

$$S^T(\omega) = S(\omega), \quad (5.6.20b)$$

$$V^T(\omega) = -U(\omega). \quad (5.6.20c)$$

We now find the inverse of matrix (5.6.17). By means of direct multiplication of the matrices it is easy to verify that the inverse matrix has the form

$$\begin{pmatrix} R^{-1} + R^{-1}UE^{-1}VR^{-1} & -R^{-1}UE^{-1} \\ -E^{-1}VR^{-1} & E^{-1} \end{pmatrix} = \begin{pmatrix} K(\omega) & M(\omega) \\ N(\omega) & L(\omega) \end{pmatrix}, \quad (5.6.21)$$

where

$$E = S - VR^{-1}U. \quad (5.6.22)$$

We suppose that the inverse matrices R^{-1} and E^{-1} exist. Using (5.6.20), we can readily verify that the matrix (5.6.22) and consequently its inverse $E^{-1} \equiv L$ are symmetric. Further, due to symmetry of E^{-1} and since $V^T = -U$, the matrices $R^{-1}UE^{-1}VR^{-1}$ and, consequently, K are symmetric. Finally, using the symmetry of the matrix E^{-1} and (5.6.20c), we easily verify that the relation $(E^{-1}VR^{-1})^T = -R^{-1}UE^{-1}$ is valid, i.e. $N^T = -M$. Thus, relations $K^T(\omega) = K(\omega)$, $L^T(\omega) = L(\omega)$ and $N^T(\omega) = -M(\omega)$, which are analogous to (5.6.20), are valid. This means that the reciprocal relation

$$\varepsilon_\alpha \varepsilon_\beta Q'_{\beta,\alpha}(\omega) = Q'_{\alpha,\beta}(\omega), \quad (5.6.23)$$

holds, which is equivalent to

$$Q_{2,1}^{t,c} = Q_{1,2}. \quad (5.6.24)$$

The condition of nondegeneracy of the matrix R used above (the condition of nondegeneracy of E follows from it and from nondegeneracy of (5.6.17)) is not a matter of principle. We can get rid of this condition by modifying the proof; thus, in the case of a degenerate matrix R we can treat this matrix as the limit of a nondegenerate matrix, use the above considerations for the “pre-limit” matrices and go to the limit. The matrices K , L , M , N will have the same symmetry properties in the limit.

Relation (5.6.24) implies a reciprocal relation of the identical form, i.e.

$$Z_{2,1}^{t,c} = Z_{1,2} \quad (5.6.25)$$

for the modified impedance.

5.6.3 Linear FDR or Nyquist's Formula

Random forces arising in a system and inducing heat fluctuations will be denoted by $\mathcal{E}_\alpha(t)$. Random internal parameters B_α are determined by both nonrandom forces $h_\alpha(t)$ and by random forces $\mathcal{E}_\alpha(t)$. The corresponding formula has the form

$$B_1 = \tilde{G}_{1,2}(h_2 + \mathcal{E}_2) + \frac{1}{2}\tilde{G}_{1,23}(h_2 + \mathcal{E}_2)(h_3 + \mathcal{E}_3) + \frac{1}{6}\tilde{G}_{1,234}(h_2 + \mathcal{E}_2)(h_3 + \mathcal{E}_3)(h_4 + \mathcal{E}_4) + \dots, \quad (5.6.26)$$

which is a generalization of (5.2.4). Here $\tilde{G}_{1,2\dots m}$ are admittances which differ very little from $G_{1,2\dots m}$. They are defined by using the condition that we must obtain (5.2.4) after averaging (5.6.26).

In the linear approximation, instead of (5.6.26) one should take the simple linear equation

$$B_1 = \tilde{G}_{1,2}(h_2 + \mathcal{E}_2). \quad (5.6.27)$$

Averaging (5.6.27) and setting $\langle \mathcal{E}_2 \rangle = 0$, we find

$$A_1 = \tilde{G}_{1,2}h_2. \quad (5.6.28)$$

If we compare (5.6.28) with equation (5.2.4) taken in the linear approximation, we obtain the equation

$$\tilde{G}_{1,2} = G_{1,2}, \quad (5.6.29)$$

which is valid in the framework of this approximation.

If we solve (5.6.27) for \mathcal{E}_2 by using (5.6.29), we arrive at

$$\mathcal{E}_1 = -h_1 + Q_{1,2}B_2. \quad (5.6.30)$$

Here according to (5.6.6a) the matrix $Q_{1,2}$ is the inverse of $G_{1,2}$. We denote the correlator of random forces by L_{12} :

$$L_{12} = \langle \mathcal{E}_1, \mathcal{E}_2 \rangle. \quad (5.6.31)$$

According to (5.6.30) we have

$$L_{12} = Q_{1,3}Q_{2,4}\langle B_3, B_4 \rangle. \quad (5.6.32)$$

Substitution of (5.3.6) into the right-hand side of (5.6.32) yields

$$\begin{aligned} L_{12} &= Q_{1,3}Q_{2,4}i\hbar\Gamma_4^-(G_{3,4} - G_{4,3}) \\ &= i\hbar\Gamma_2^-\mathcal{Q}_{1,3}Q_{2,4}(G_{3,4} - G_{4,3}). \end{aligned} \quad (5.6.33)$$

But $Q_{1,3}G_{3,4}$ (and also $Q_{2,4}G_{4,3}$) is the identity matrix because of (5.6.6a). Therefore (5.6.33) takes the form

$$L_{12} = -i\hbar\Gamma_2^-(Q_{1,2} - Q_{2,1}). \quad (5.6.34)$$

This is the linear FDR of the third kind. Applying (5.6.10) and (5.3.93), we can also write (5.6.34) in the form

$$L_{12} = kT\Theta_2^-(Z_{1,2} + Z_{2,1}) \quad (5.6.35)$$

or in the symmetrized form

$$L_{12}^{\text{sym}} \equiv \frac{1}{2}(L_{12} + L_{21}) = kT\Theta_2(Z_{1,2} + Z_{2,1}). \quad (5.6.36)$$

In the nonquantum limit $\hbar \rightarrow 0$, the operator Θ^- goes to unity, and (5.6.35) implies formula $L_{12} = kT(Z_{1,2} + Z_{2,1})$ or $L_{12} = kT(Z_{1,2} + Z_{1,2}^{t,c})$ if we use (5.6.25). In the spectral representation this formula is of the form

$$\beta L_{\alpha\gamma}(\omega_1, \omega_2) = Z_{\alpha,\gamma}(\omega_1, \omega_2) + \varepsilon_\alpha \varepsilon_\gamma Z_{\alpha,\gamma}^*(\omega_1, \omega_2). \quad (5.6.37)$$

When all the parameters B_α have the same time parity, i.e. when all $\varepsilon_\alpha, \varepsilon_\beta = 1$, (5.6.37) can be written as

$$L_{\alpha\beta}(\omega_1, \omega_2) = 2kT \operatorname{Re}\{Z_{\alpha,\beta}(\omega_1, \omega_2)\}. \quad (5.6.38)$$

Using equation

$$Z_{\alpha,\beta}(\omega_1, \omega_2) = Z'_{\alpha,\beta}(-\omega_1)\delta(\omega_1 + \omega_2), \quad (5.6.39)$$

which is analogous to (5.2.29), and introducing the spectral density $S_{\alpha\beta}^{(\mathcal{E})}(\omega)$ of random forces $\mathcal{E}_\alpha(t)$ by the equation

$$L_{\alpha\beta}(\omega_1, \omega_2) = S_{\alpha\beta}^{(\mathcal{E})}(\omega_1)\delta(\omega_1 + \omega_2) \quad (5.6.40)$$

formula (5.6.38) can also be written in the equivalent form

$$S_{\alpha\beta}^{(\mathcal{E})}(\omega) = 2kT \operatorname{Re}\{Z'_{\alpha,\beta}(\omega)\}. \quad (5.6.41)$$

Formula (5.6.41) was obtained by Nyquist in 1928 [5.10]. Historically, this was the first general result of linear nonequilibrium thermodynamics.

If we return to the quantum variant, then formula

$$S_{\alpha\beta}^{(\mathcal{E})}(\omega) = 2kT \Theta(i\omega) \operatorname{Re}\{Z'_{\alpha,\beta}(\omega)\} = \hbar\omega \coth(\hbar\omega/2kT) \operatorname{Re}\{Z'_{\alpha,\beta}(\omega)\} \quad (5.6.42)$$

holds instead of (5.6.41). Here $S_{\alpha\beta}^{(\mathcal{E})}(\omega)$ is defined by

$$\frac{1}{2}[L_{\alpha\beta}(\omega_1, \omega_2) + L_{\beta\alpha}(\omega_2, \omega_1)] = S_{\alpha\beta}^{(\mathcal{E})}(\omega_1)\delta(\omega_1 + \omega_2). \quad (5.6.43)$$

5.6.4 Correlators of Random Forces in the Nonlinear Case: Their Relation to the Functions $G\dots$

In the nonlinear case, the equations

$$\langle \hat{B}_1, \hat{B}_2 \rangle = G_{12} + G_{12,3}h_3 + \frac{1}{2}G_{12,34}h_3h_4 + \dots, \quad (5.6.44a)$$

$$\langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle = G_{123} + G_{123,4}h_4 + \dots. \quad (5.6.44b)$$

$$\langle \hat{B}_1, \hat{B}_2, \hat{B}_3, \hat{B}_4 \rangle = G_{1234} + \dots \quad (5.6.44c)$$

hold in addition to (5.2.4). The functions G_{12} , G_{123} , $G_{12,3}$ and the others are connected with admittances $G_{1,2}$, $G_{1,23}, \dots$ through FDRs of the second kind.

Let us introduce correlators of the random forces $\hat{\mathcal{E}}_1$. By analogy with (5.2.4) and (5.6.44) we represent these correlators in the form of an expansion in terms of nonrandom external forces

$$\begin{aligned} \langle \hat{\mathcal{E}}_1 \rangle &= L_1 + L_{1,2}h_2 + \frac{1}{2}L_{1,23}h_2h_3 \\ &\quad + \frac{1}{6}L_{1,234}h_2h_3h_4 + \dots, \end{aligned} \quad (5.6.45a)$$

$$\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2 \rangle = L_{12} + L_{12,3}h_3 + \frac{1}{2}L_{12,34}h_3h_4 + \dots, \quad (5.6.45b)$$

$$\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3 \rangle = L_{123} + L_{123,4}h_4 + \dots, \quad (5.6.45c)$$

$$\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3, \hat{\mathcal{E}}_4 \rangle = L_{1234} + \dots. \quad (5.6.45d)$$

The functions $L\dots$ defined by (5.6.45) can be related to the functions $G\dots$. For this purpose we solve (5.6.26) for $\hat{\mathcal{E}}$. This yields

$$\hat{\mathcal{E}}_1 = -h_1 + \tilde{Q}_{1,2}\hat{B}_2 + \frac{1}{2}\tilde{Q}_{1,23}\hat{B}_2\hat{B}_3 + \frac{1}{6}\tilde{Q}_{1,234}\hat{B}_2\hat{B}_3\hat{B}_4 + \dots. \quad (5.6.46)$$

The impedances $\tilde{Q}_{1,2\dots m}$ are connected to the admittances $\tilde{G}_{1,2\dots m}$ by formulas of the same type (5.6.6) as those that connect $Q_{1,2\dots m}$ to $G_{1,2\dots m}$.

Averaging (5.6.46) and using (5.2.4) and (5.6.44, 45), we arrive at

$$\begin{aligned} L_1 + h_1 + L_{1,2}h_2 + \frac{1}{2}L_{1,23}h_2h_3 + \dots \\ = \tilde{Q}_{1,2}(G_{2,3}h_3 + \frac{1}{2}G_{2,34}h_3h_4 + \dots) \\ + \frac{1}{2}\tilde{Q}_{1,23}(G_{2,4}h_4G_{3,5}h_5 + G_{23} + G_{23,4}h_4 + \frac{1}{2}G_{23,45}h_4h_5 + \dots) \\ + \frac{1}{6}\tilde{Q}_{1,234}(G_{234} + G_{234,5}h_5 + \dots) + \dots. \end{aligned} \quad (5.6.47)$$

Hence, separating out the terms having different orders in h , we obtain

$$L_1 = \frac{1}{2}\tilde{Q}_{1,23}G_{23} + \frac{1}{6}\tilde{Q}_{1,234}G_{234} + \dots, \quad (5.6.48a)$$

$$h_1 + L_{1,2}h_2 = \tilde{Q}_{1,2}G_{2,3}h_3 + \frac{1}{2}\tilde{Q}_{1,23}G_{23,4}h_4 + \frac{1}{6}\tilde{Q}_{1,234}G_{234,5}h_5 + \dots, \quad (5.6.48b)$$

$$L_{1,45} = \tilde{Q}_{1,2}G_{2,45} + \tilde{Q}_{1,23}G_{2,4}G_{3,5} + \frac{1}{2}\tilde{Q}_{1,23}G_{23,45} + \dots. \quad (5.6.48c)$$

Formula (5.6.48a) can be used for determining L_1 , formulas (5.6.48b,c) for determining $\tilde{Q}_{1,2}$, $\tilde{Q}_{1,23}$ respectively, etc. Here one must also use other equations which will be given later. The determination of $\tilde{Q}_{1,2}$, $\tilde{Q}_{1,23}$ can be carried out by successive approximations starting with the following values of the zeroth-order approximation:

$$\tilde{Q}_{1,2} = Q_{1,2}, \quad \tilde{Q}_{1,23} = Q_{1,23}, \quad \tilde{Q}_{1,234} = Q_{1,234}. \quad (5.6.49)$$

In order to find the correlator $\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2 \rangle$, we now apply (5.6.46). We have

$$\begin{aligned} \langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2 \rangle &= \tilde{Q}_{1,3}\tilde{Q}_{2,4}\langle \hat{B}_3, \hat{B}_4 \rangle + \frac{1}{2}\tilde{Q}_{1,3}\tilde{Q}_{2,45}\langle \hat{B}_3, \hat{B}_4\hat{B}_5 \rangle \\ &\quad + \frac{1}{2}\tilde{Q}_{1,34}\tilde{Q}_{2,5}\langle \hat{B}_3\hat{B}_4, \hat{B}_5 \rangle + \dots. \end{aligned} \quad (5.6.50)$$

Note that $\langle \hat{B}_3, \hat{B}_4\hat{B}_5 \rangle = \langle \hat{B}_3, \hat{B}_4 \rangle \langle \hat{B}_5 \rangle + \langle \hat{B}_3, \hat{B}_5 \rangle \langle \hat{B}_4 \rangle + \dots$. The dots in (5.6.50) denote further terms, which give relatively small contributions, i.e. of the order of $(kT)^2$ and of higher orders (we assume that $\hbar\omega \sim kT$ in such estimates). Using (5.2.4) and (5.6.44), we obtain from (5.6.50)

$$\begin{aligned} \langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2 \rangle &= \tilde{Q}_{1,3}\tilde{Q}_{2,4}(G_{34} + G_{34,5}h_5 + \dots) \\ &\quad + \frac{1}{2}\tilde{Q}_{1,3}\tilde{Q}_{2,45}(G_{34}G_{5,6} + G_{35}G_{4,6})h_6 \\ &\quad + \frac{1}{2}\tilde{Q}_{1,34}\tilde{Q}_{2,5}(G_{35}G_{4,6} + G_{45}G_{3,6})h_6 + \dots. \end{aligned} \quad (5.6.51)$$

Comparing (5.6.51) with (5.6.45), in the approximation corresponding to (5.6.49) we arrive at

$$L_{12} = Q_{1,3}Q_{2,4}G_{34}, \quad (5.6.52a)$$

$$L_{12,6} = Q_{1,3}Q_{2,4}G_{34,6} + Q_{1,3}Q_{2,45}G_{34}G_{5,6} + Q_{1,34}Q_{2,5}G_{35}G_{4,6}. \quad (5.6.52b)$$

Here the symmetry $Q_{2,45} = Q_{2,54}$ has been used.

We now proceed to calculate the triple correlator $\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3 \rangle$. We shall take into account terms of order up to $(kT)^2$ and omit the terms of higher orders. Furthermore, we can now set $h(t) \equiv 0$. Applying the rules for calculation of the correlator (these were given in Sect. 2.1.2), we obtain

$$\begin{aligned} \langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3 \rangle &= \tilde{Q}_{1,4}\tilde{Q}_{2,5}\tilde{Q}_{3,6}\langle \hat{B}_4, \hat{B}_5, \hat{B}_6 \rangle + \frac{1}{2}\tilde{Q}_{1,47}\tilde{Q}_{2,5}\tilde{Q}_{3,6} \\ &\quad \times (\langle \hat{B}_4, \hat{B}_5 \rangle \langle \hat{B}_7, \hat{B}_6 \rangle + \langle \hat{B}_7, \hat{B}_5 \rangle \langle \hat{B}_4, \hat{B}_6 \rangle) \\ &\quad + \tilde{Q}_{1,4}\tilde{Q}_{2,57}\tilde{Q}_{3,6}\langle \hat{B}_4, \hat{B}_5 \rangle \langle \hat{B}_7, \hat{B}_6 \rangle \\ &\quad + \tilde{Q}_{1,4}\tilde{Q}_{2,5}\tilde{Q}_{3,67}\langle \hat{B}_4, \hat{B}_6 \rangle \langle \hat{B}_5, \hat{B}_7 \rangle + \dots. \end{aligned} \quad (5.6.53)$$

Hence using (5.6.44, 45), we get in the approximation (5.6.49)

$$\begin{aligned} L_{123} = & Q_{1,4}Q_{2,5}Q_{3,6}G_{456} + Q_{1,47}Q_{2,5}Q_{3,6}G_{45}G_{76} \\ & + Q_{1,4}Q_{2,57}Q_{3,6}G_{45}G_{76} + Q_{1,4}Q_{2,5}Q_{3,67}G_{46}G_{57}. \end{aligned} \quad (5.6.54)$$

The expressions on the right-hand sides of (5.6.52, 54) have a relative error equal to kT .

5.6.5 Formulas for $L_{12,3}$ and L_{123}

The functions G_{34} , $G_{34,5}$, G_{456} in (5.6.52, 54) can be expressed in terms of admittances by using (5.3.6, 65, 89). Substitution of (5.3.6, 89) into (5.6.52b) gives

$$\begin{aligned} L_{12,6} = & i\hbar \{ Q_{1,3}Q_{2,4}[\Gamma_4^-Q_{3,46} + \Gamma_3^+G_{4,36} - (\Gamma_3 + \Gamma_4)G_{6,34}^{\text{t.c.}}] \\ & - Q_{1,3}\Gamma_3^+(G_{3,4} - G_{4,3})Q_{2,45}G_{5,6} \\ & + Q_{2,5}\Gamma_5^-(G_{3,5} - G_{5,3})Q_{1,34}G_{4,6} \}. \end{aligned} \quad (5.6.55)$$

If we use the shortened notation of (5.6.11), then (5.6.55) takes the form

$$\begin{aligned} L_{12,3} = & i\hbar \{ Q_1Q_2[\Gamma_2^-G_{1,23} + \Gamma_1^+G_{2,13} - (\Gamma_1 + \Gamma_2)G_{3,21}^{\text{t.c.}}] \\ & - \Gamma_1^+Q_1(G_1 - G_1^T)Q_{2,13}G_3 + \Gamma_2^-Q_2(G_2^T - G_2)Q_{1,23}G_3 \}. \end{aligned} \quad (5.6.56)$$

We now take into account the relations

$$QG = 1, \quad G_{1,23} = -G_1G_2^TG_3^TQ_{1,23} \quad (5.6.57)$$

according to (5.6.6, 11). Performing the operation of time conjugation, we have

$$\begin{aligned} G_{1,23}^{\text{t.c.}} &= -(G_1G_2^TG_3^TQ_{1,23})^{\text{t.c.}} \\ &= -G_1^{\text{t.c.}}(G_2^{\text{t.c.}})^T(G_3^{\text{t.c.}})^TQ_{1,23}^{\text{t.c.}} \\ &= -G_1^TG_2G_3Q_{1,23}^{\text{t.c.}} \end{aligned} \quad (5.6.58)$$

by virtue of equation $G_{1,2}^{\text{t.c.}} = G_{1,2}^T$, which is equivalent to (5.3.46). Using (5.6.57, 58), we obtain from (5.6.56)

$$\begin{aligned} L_{12,3} = & i\hbar \{ -\Gamma_2^-Q_2G_2^TQ_{1,23} - \Gamma_1^+Q_1G_1^TQ_{2,13} + (\Gamma_1 + \Gamma_2)Q_{3,21}^{\text{t.c.}} \\ & - \Gamma_1^+(1 - Q_1G_1^T)Q_{2,13} + \Gamma_2^-(Q_2G_2^T - 1)Q_{1,23} \} G_3. \end{aligned} \quad (5.6.59)$$

Hence after cancellations we get

$$L_{12,3} = -i\hbar \{ \Gamma_2^-Q_{1,23} + \Gamma_1^+Q_{2,13} - (\Gamma_1 + \Gamma_2)Q_{3,21}^{\text{t.c.}} \} G_3. \quad (5.6.60)$$

Let us now proceed to (5.6.54). Substitution of (5.3.6, 65) into (5.6.54) yields

$$\begin{aligned} L_{123} = & -\hbar^2 \{ Q_1Q_2Q_3[\Gamma_2^-\Gamma_3^-(G_{1,23} + G_{1,23}^{\text{t.c.}}) + \Gamma_1^+\Gamma_3^-(G_{2,13} + G_{2,13}^{\text{t.c.}}) \\ & + \Gamma_1^+\Gamma_2^+(G_{3,12} + G_{3,12}^{\text{t.c.}})] + \Gamma_2^-\Gamma_3^-\Gamma_2(G_2^T - G_2)Q_3(G_3^T - G_3)Q_{1,23} \\ & + \Gamma_1^+\Gamma_3^-\Gamma_1(G_1^T - G_1)Q_3(G_3^T - G_3)Q_{2,13} \\ & + \Gamma_1^+\Gamma_2^+\Gamma_1(G_1^T - G_1)Q_2(G_2^T - G_2)Q_{3,12} \}. \end{aligned} \quad (5.6.61)$$

Using (5.6.57, 58), we express $G_{1,23}$ in terms of $Q_{1,23}$. After cancellations we arrive at

$$\begin{aligned} L_{123} = & -\hbar^2 \left\{ -\Gamma_2^- \Gamma_3^- X_1 Q_{1,23}^{t,c} - \Gamma_1^+ \Gamma_3^- X_2 Q_{2,13}^{t,c} - \Gamma_1^+ \Gamma_2^+ X_3 Q_{3,12}^{t,c} \right. \\ & + \Gamma_2^- \Gamma_3^- (1 - X_2 - X_3) Q_{1,23} + \Gamma_1^+ \Gamma_3^- (1 - X_1 - X_3) Q_{2,13} \\ & \left. + \Gamma_1^+ \Gamma_2^+ (1 - X_1 - X_2) Q_{3,12} \right\}, \end{aligned} \quad (5.6.62)$$

where we have designated $X = QG^T$, i.e.

$$X_{12} = Q_{1,3} G_{2,3}. \quad (5.6.63)$$

The matrix (5.6.63) appearing in (5.6.62) is somewhat strange. Such a matrix did not appear in the relations obtained in Sect. 5.3. One can conclude, from the presence of the matrix (5.6.63) in (5.6.62), that (5.6.62) cannot be regarded as a final fluctuation–dissipation relation.

5.6.6 The Functions $Q_{...}$ and the Stochastic Representation of Random Forces

In the linear–quadratic approximation one should take the following stochastic representation of the random forces

$$\mathcal{E}_1 = M_1 + \sum_{\sigma} [S_{12}^{(\sigma)} \xi_2^{(\sigma)} + S_{123}^{(\sigma)} \xi_2^{(\sigma)} B_3], \quad (5.6.64)$$

where M_1 is independent of time t_1 , and $\xi_i^{(\sigma)}$ are the statistically independent random functions, which are operators in the quantum case. They have zero means and their correlators are

$$\begin{aligned} \langle \xi_1^{(\sigma)}, \xi_2^{(\sigma)} \rangle &= R_{12}^{(\sigma)}, \\ \langle \xi_1^{(\sigma)}, \xi_2^{(\sigma)}, \xi_3^{(\sigma)} \rangle &= R_{123}^{(\sigma)}, \\ \langle \xi_1^{(\sigma)}, \xi_2^{(\sigma)}, \xi_3^{(\sigma)}, \xi_4^{(\sigma)} \rangle &= R_{1234}^{(\sigma)}, \dots \end{aligned} \quad (5.6.65)$$

All cross-correlators are assumed to be equal to zero due to their statistical independence. In (5.6.64) $S_{12}^{(\sigma)}$ and $S_{123}^{(\sigma)}$ are some functions.

Expression (5.6.64) should be considered in combination with (5.6.26). Correlations between B_3 and $\xi_2^{(\sigma)}$ come into existence as a consequence of (5.6.26). If we however regard expression (5.6.64) as an independent one before its substitution into (5.6.26), then the functions B_3 in (5.6.64) can be regarded as independent variables. Fixing them, we introduce the functions $Q_{...}$ by means of the equations

$$\begin{aligned} \langle \mathcal{E}_1 \rangle_B &= Q_1, \\ \langle \mathcal{E}_1, \mathcal{E}_2 \rangle_B &= Q_{12} + Q_{12,3} B_3 + \frac{1}{2} Q_{12,34} B_3 B_4 + \dots, \\ \langle \mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3 \rangle_B &= Q_{123} + Q_{123,4} B_4 + \dots, \\ \langle \mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3, \mathcal{E}_4 \rangle_B &= Q_{1234} + \dots. \end{aligned} \quad (5.6.66)$$

Here the terms with four-subscript functions are added for the sake of completeness. To calculate these functions, one must consider expressions more complex than (5.6.64). This expression will be considered in Sect. 5.7. The subscript B in (5.6.66) indicates that the function $B_a(\cdot)$ is taken as the set of independent

arguments and fixed. According to this, equations (5.6.66) differ from equations (5.6.45), in that B_1 is related to \mathcal{E}_1 and consequently to $\xi^{(\sigma)}$ by (5.6.26) or (5.6.46).

The stochastic expression (5.6.64) as well as analogous expressions for higher nonlinearities are linear with respect to the random functions $\xi_1^{(\sigma)}$, which have zero mean values. Therefore, $\langle \mathcal{E}_1 \rangle_B$ is independent of B , and in all approximations we have

$$Q_1 = M_1 . \quad (5.6.67)$$

Using (5.6.64, 65), we easily find the two- and three-subscript functions appearing in (5.6.66):

$$Q_{12} = \sum_{\sigma} S_{13}^{(\sigma)} S_{24}^{(\sigma)} R_{34}^{(\sigma)} \equiv \sum_{\sigma} S_1^{(\sigma)} S_2^{(\sigma)} R_{12}^{(\sigma)} , \quad (5.6.68a)$$

$$Q_{12,3} = \sum_{\sigma} [S_{143}^{(\sigma)} S_2^{(\sigma)} R_{42}^{(\sigma)} + S_1^{(\sigma)} S_{243}^{(\sigma)} R_{14}^{(\sigma)}] , \quad (5.6.68b)$$

$$Q_{123} = \sum_{\sigma} S_1^{(\sigma)} S_2^{(\sigma)} S_3^{(\sigma)} R_{123}^{(\sigma)} . \quad (5.6.68c)$$

The four-subscript functions $Q_{...}$ will be considered later (Sect. 5.7). The definition of functions $Q_{...}$ is to some extent analogous to the definitions (5.1.92, 93) of the functions $\Phi_{...}$ in Sect. 5.1.

5.6.7 Quadratic FDRs of the Third Kind

We now find the correlators (5.6.45) and the functions $L_{...}$ by combining (5.6.64) with (5.6.26). Substituting equation (5.6.26) taken in the approximation (5.6.49) into (5.6.64), we arrive at

$$\begin{aligned} \mathcal{E}_1 = M_1 &+ \sum_{\sigma} [S_1^{(\sigma)} \xi_1^{(\sigma)} + S_{123}^{(\sigma)} \xi_2^{(\sigma)} G_{3,4}(h_4 + \mathcal{E}_4) \\ &+ \frac{1}{2} S_{123}^{(\sigma)} \xi_2^{(\sigma)} G_{3,45}(h_4 + \mathcal{E}_4)(h_5 + \mathcal{E}_5) + \dots] . \end{aligned} \quad (5.6.69)$$

Equations of the type (5.6.69) can now be substituted for \mathcal{E}_1 into the right-hand side of (5.6.69) by iterations. Thus, one can express \mathcal{E}_1 in terms of $\xi_1^{(\sigma)}$ and h_1 to any desired degree of accuracy. Then one can find the correlators (5.6.45) using (5.6.65). In order to find $\langle \mathcal{E}_1, \mathcal{E}_2 \rangle$ in the first nonvanishing approximation, i.e. with an error of the order of $(kT)^2$, it is sufficient to take

$$\mathcal{E}_1 = M_1 + \sum_{\sigma} [S_1^{(\sigma)} \xi_1^{(\sigma)} + S_{123}^{(\sigma)} \xi_2^{(\sigma)} G_{3,4} h_4] . \quad (5.6.70)$$

Calculating the correlator according to ordinary rules and using (5.6.65), we obtain

$$\langle \mathcal{E}_1, \mathcal{E}_2 \rangle = \sum_{\sigma} [S_1^{(\sigma)} S_2^{(\sigma)} R_{12}^{(\sigma)} + (S_{143}^{(\sigma)} S_2^{(\sigma)} R_{42}^{(\sigma)} + S_1^{(\sigma)} S_{243}^{(\sigma)} R_{14}^{(\sigma)}) G_3 h_3] . \quad (5.6.71)$$

Because of (5.6.68a, b) this may be written as

$$\langle \mathcal{E}_1, \mathcal{E}_2 \rangle = Q_{12} + Q_{12,3} G_3 h_3 . \quad (5.6.72)$$

Hence, according to (5.6.45) we have

$$L_{12} = Q_{12}, \quad (5.6.73a)$$

$$L_{12,3} = Q_{12,3} G_3. \quad (5.6.73b)$$

As a consequence of (5.6.34, 60), equations (5.6.73) give

$$Q_{12} = -i\hbar\Gamma_2^-(Q_{1,2} - Q_{2,1}), \quad (5.6.74a)$$

$$Q_{12,3} = -i\hbar[\Gamma_2^- Q_{1,23} + \Gamma_1^+ Q_{2,13} - (\Gamma_1 + \Gamma_2) Q_{3,21}^{tc}]. \quad (5.6.74b)$$

Equation (5.6.74a) is the equivalent form of the linear FDR, and (5.6.74b) is one of the two quadratic FDRs of the third kind. In order to obtain the second quadratic FDR, we shall find the triple correlator $\langle \mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3 \rangle = L_{123}$ taken at $h = 0$ using (5.6.69). Here we must take into account the terms of order $(kT)^2$ and omit those of higher orders. It is sufficient to consider the equation

$$\mathcal{E}_1 = M_1 + \sum_{\sigma} S_1^{(\sigma)} \xi_1^{(\sigma)} + \sum_{\sigma, \tau} S_{123}^{(\sigma)} \xi_2^{(\sigma)} G_{3,4} S_4^{(\tau)} \xi_4^{(\tau)}. \quad (5.6.75)$$

expressing \mathcal{E}_1 in terms of $\xi^{(\sigma)}$. Using (5.6.75, 65), we obtain

$$\begin{aligned} L_{123} = & \sum_{\sigma} S_1^{(\sigma)} S_2^{(\sigma)} S_3^{(\sigma)} R_{123}^{(\sigma)} + \sum_{\sigma, \tau} [S_{145}^{(\sigma)} P_{23} S_2^{(\sigma)} R_{42}^{(\sigma)} G_5 S_5^{(\tau)} S_3^{(\tau)} R_{53}^{(\tau)} \\ & + S_{245}^{(\sigma)} (S_1^{(\sigma)} R_{14}^{(\sigma)} G_5 S_5^{(\tau)} S_3^{(\tau)} R_{53}^{(\tau)} + S_3^{(\sigma)} R_{43}^{(\sigma)} G_5 S_5^{(\tau)} S_1^{(\tau)} R_{15}^{(\tau)}) \\ & + S_{345}^{(\sigma)} P_{12} S_1^{(\sigma)} R_{14}^{(\sigma)} G_5 S_5^{(\tau)} S_2^{(\tau)} R_{25}^{(\tau)}]. \end{aligned} \quad (5.6.76)$$

Taking into account (5.6.68) and designating

$$Q_{12,3}^- = \sum_{\sigma} S_{143}^{(\sigma)} S_2^{(\sigma)} R_{42}^{(\sigma)}, \quad (5.6.77)$$

$$Q_{12,3}^+ = \sum_{\sigma} S_{143}^{(\sigma)} S_2^{(\sigma)} R_{24}^{(\sigma)},$$

so that

$$Q_{12,3} = Q_{12,3}^- + Q_{21,3}^+, \quad (5.6.78)$$

we can reduce (5.6.76) to the form

$$L_{123} = Q_{123} + Q_{12,5} G_5 Q_{53} + Q_{13,5}^- G_5 Q_{52} + Q_{31,5}^+ G_5 Q_{25} + Q_{23,5} G_5 Q_{15}. \quad (5.6.79)$$

Using (5.6.63), we get, by virtue of (5.6.74a),

$$\begin{aligned} G_5 Q_{53} &= -i\hbar\Gamma_3^- G_5 (Q_{5,3} - Q_{3,5}) = -i\hbar\Gamma_3^- (\delta_{53} - X_{35}), \\ G_5 Q_{15} &= -i\hbar\Gamma_5^- G_5 (Q_{1,5} - Q_{5,1}) \\ &= -i\hbar\Gamma_5^- (X_{15} - \delta_{51}) = i\hbar\Gamma_1^+ (X_{15} - \delta_{51}) \end{aligned} \quad (5.6.80)$$

and therefore

$$Q_{1,25} G_5 Q_{53} = -i\hbar\Gamma_3^- Q_{1,23} (1 - X_3^T) = i\hbar\Gamma_3^- (X_3 - 1) Q_{1,23}, \quad (5.6.81)$$

$$Q_{23,5} G_5 Q_{15} = i\hbar\Gamma_1^+ (X_1 - 1) Q_{23,1}.$$

Considering (5.6.81) and substituting (5.6.74b) into the right-hand side of (5.6.79), we find from (5.6.79)

$$\begin{aligned} L_{123} = & Q_{123} + \hbar^2 \{ \Gamma_3^- (X_3 - 1) [\Gamma_2^- Q_{1,23} + \Gamma_1^+ Q_{2,13} - (\Gamma_1^+ + \Gamma_2^-) Q_{3,21}^{t.c.}] \\ & + \Gamma_1^+ (X_1 - 1) [\Gamma_3^- Q_{2,31} + \Gamma_2^+ Q_{3,21} - (\Gamma_2^+ + \Gamma_3^-) Q_{1,23}^{t.c.}] \} \\ & + i\hbar (X_2 - 1) [\Gamma_2^- Q_{13,2}^- + \Gamma_2^+ Q_{31,2}^+] . \end{aligned} \quad (5.6.82)$$

Here one can replace the expression $(\Gamma_1^+ + \Gamma_2^-) \Gamma_3^- Q_{3,21}^{t.c.}$ by the expression $- \Gamma_1^+ \Gamma_2^+ Q_{3,21}^{t.c.}$, which is equal to the former on account of (5.2.104), and likewise the expression $\Gamma_1^+ (\Gamma_2^+ + \Gamma_3^-) Q_{1,23}^{t.c.}$ can be replaced by $- \Gamma_1^+ \Gamma_3^- Q_{1,23}^{t.c.}$. We now equate the resulting expression to that appearing on the right-hand side of (5.6.62), where $\Gamma_1^+ \Gamma_3^- Q_{2,13}^{t.c.}$ is taken instead of $- (\Gamma_1^+ \Gamma_2^+ + \Gamma_2^- \Gamma_3^-) Q_{2,13}^{t.c.}$. The terms with X_3 and X_1 immediately cancel out. The terms with the “strange” operator X_2 drop out if and only if the formula

$$\begin{aligned} & -i\hbar [\Gamma_2^- \Gamma_3^- Q_{1,23} + \Gamma_1^+ \Gamma_2^+ Q_{3,12} - (\Gamma_1^+ \Gamma_2^+ + \Gamma_2^- \Gamma_3^-) Q_{2,13}^{t.c.}] \\ & = \Gamma_2^- Q_{13,2}^- + \Gamma_2^+ Q_{31,2}^+ . \end{aligned} \quad (5.6.83)$$

is valid. But since

$$-i\hbar [\Gamma_3^- Q_{1,23} + \Gamma_1^+ Q_{3,12} - (\Gamma_1^+ + \Gamma_2^-) Q_{2,13}^{t.c.}] = Q_{13,2}^- + Q_{31,2}^+ = Q_{13,2} \quad (5.6.84)$$

by virtue of (5.6.74b), in the quantum case (5.6.83) is equivalent to the equations

$$Q_{13,2}^\pm = -i\hbar \Gamma_3^\pm (Q_{1,32} - Q_{2,13}^{t.c.}) , \quad (5.6.85)$$

which are analogous to (5.5.71). In the nonquantum case (5.6.83) does not differ from (5.6.84), so that the terms with X_2 unconditionally cancel out.

If (5.6.83) is valid, then using (5.2.104) once more, we obtain after cancellations

$$\begin{aligned} Q_{123} = & \hbar^2 [\Gamma_2^- \Gamma_3^- (Q_{1,23} + Q_{1,23}^{t.c.}) + \Gamma_1^+ \Gamma_3^- (Q_{2,13} + Q_{2,13}^{t.c.}) \\ & + \Gamma_1^+ \Gamma_2^+ (Q_{3,12} + Q_{3,12}^{t.c.})] . \end{aligned} \quad (5.6.86)$$

This relation is the second quadratic FDR. We see that (5.6.74, 86) have the same structure as the relations of the second kind (5.3.6, 65, 89), but impedances enter into the right-hand sides of (5.6.74, 86) instead of admittances. As we see, the function (5.6.86) is invariant under time conjugation just like the correlator G_{123} .

5.6.8 Determination of L_1 and Q_1

The formula that expresses Q_1 in terms of impedances or admittances must also be regarded as a quadratic relation. In order to derive it, we use (5.6.48a) in the approximation (5.6.49). Taking into account only the term of the order of kT and omitting terms of higher orders, we arrive at

$$L_1 = \frac{1}{2} Q_{1,23} G_{23} . \quad (5.6.87)$$

If we substitute (5.5.6) into (5.6.87), we obtain

$$L_1 = \frac{1}{2} i\hbar Q_{1,23} \Gamma_3^- (G_{2,3} - G_{3,2}) . \quad (5.6.88)$$

Using the symmetry $G_{1,23} = G_{1,32}$ and also (5.2.103), the last equation can be transformed to

$$L_1 = \frac{1}{2}i\hbar Q_{1,23}(\Gamma_2^- - \Gamma_3^-)G_{3,2} = \frac{1}{2}i\hbar Q_{1,23}(\Gamma_2^- + \Gamma_2^+)G_{3,2}. \quad (5.6.89)$$

On the other hand, on account of (5.6.45a) taken at $\hbar = 0$ the value of L_1 can be obtained with the same accuracy by averaging (5.6.75). This yields

$$L_1 = M_1 + \sum_{\sigma} S_{123}^{(\sigma)} S_4^{(\sigma)} R_{24}^{(\sigma)} G_{3,4} = M_1 + \sum_{\sigma} S_{143}^{(\sigma)} S_2^{(\sigma)} R_{42}^{(\sigma)} G_{3,2}. \quad (5.6.90)$$

Hence using (5.6.77, 85) we have

$$L_1 = M_1 + Q_{12,3}^- G_{3,2} = M_1 - i\hbar[\Gamma_2^-(Q_{1,23} - Q_{3,12}^{t.c.})]G_{3,2}. \quad (5.6.91)$$

Transferring the operator Γ_2^- to the right of $(Q_{1,23} - Q_{3,12}^{t.c.})$ by using the formula $[\Gamma^-(p)]^T = \Gamma^-(p) = -\Gamma^+(p)$, we have

$$L_1 = M_1 + i\hbar(Q_{1,23} - Q_{3,12}^{t.c.})\Gamma_2^+ G_{3,2}. \quad (5.6.92)$$

Comparing (5.6.92) with (5.6.89), we get

$$Q_1 = M_1 = i\hbar(-\frac{1}{2}Q_{1,23} + Q_{3,12}^{t.c.}\Gamma_2^+)G_{3,2}, \quad (5.6.93)$$

where (5.6.67) is used. We now pass from $Q_{1,23}$, $G_{3,2}$ to the modified functions $Z_{1,23}$, $Y_{3,2}$. Since $Q_{1,23} = Z_{1,23}p_2p_3$, $p_3G_{3,2} = Y_{3,2}$, we obtain from (5.6.93)

$$Q_1 = -\frac{1}{2}i\hbar Z_{1,23}p_2 Y_{3,2} + kTZ_{3,12}^{t.c.}\Theta_2^+ p_1 G_{3,2}, \quad (5.6.94)$$

where $\Theta_2^+ = i\hbar\beta p_2\Gamma_2^+$. Transposing the operator $p_1 = \partial/\partial t_1$ in the second term to the left according to the rule (5.6.10), we write this term in more detail:

$$\begin{aligned} kTZ_{3,12}^{t.c.}\Theta_2^+ p_1 G_{3,2} &= -kT \frac{\partial}{\partial t_1} \int \varepsilon_{\alpha_1} \varepsilon_{\alpha_2} \varepsilon_{\alpha_3} Z_{\alpha_3, \alpha_2 \alpha_1}(-t_3; -t_2, -t_1) \\ &\quad \times [\Theta_2^+ G_{\alpha_3, \alpha_2}(t_3, t_2)] dt_2 dt_3. \end{aligned} \quad (5.6.95)$$

If the integral in (5.6.95) converges, then it is equal to a number since $Z_{3,12}$ and $G_{3,2}$ depend only on time differences $t_3 - t_2$ and $t_3 - t_1$. This number is equal to zero in the nonquantum case due to the causality law. Differentiation of the integral with respect to t_1 gives zero, and therefore the term (5.6.95) vanishes. Consequently, (5.6.94) takes the form

$$Q_1 = -\frac{1}{2}i\hbar Q_{1,23} G_{3,2} = -\frac{1}{2}i\hbar Z_{1,23}p_2 Y_{3,2}. \quad (5.6.96)$$

We see that in the nonquantum case (5.6.96) is equal to zero, i.e. we have

$$Q_1 = M_1 = 0. \quad (5.6.97)$$

In the quantum case M_1 is not equal to zero since the averaging of (5.6.75) for $M_1 = 0$ gives a complex quantity, but due to M_1 this complex average becomes a real quantity. If instead of (5.6.64) we take the symmetrized expression i.e. the Hermitian expression

$$\mathcal{E}_1 = M_1 + \sum_{\sigma} S_1^{(\sigma)} \xi_1^{(\sigma)} + \frac{1}{2} \sum_{\sigma} S_{123}^{(\sigma)} [\xi_2^{(\sigma)}, B_3]_+, \quad (5.6.98)$$

then $M_1 = Q_1$ can be equal to zero in the quantum case.

Approximation (5.6.49) is insufficient for deriving more accurate relations than (5.6.74, 86, 96). In order to calculate the values of $\tilde{Q}_{1,2,\dots}$ more accurately, one should use an equation of the type (5.6.69) (but more accurate) to calculate the functions $L_{1,2}, L_{1,23}, \dots$ which are defined by (5.6.45a), and then one should use (5.6.48b, c), etc.

5.6.9 Another Form of FDRs of the Third Kind

Instead of (5.6.66) one can take the equivalent equations

$$\langle \hat{\mathcal{E}}_1 \rangle_J = Z_1, \quad (5.6.99a)$$

$$\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2 \rangle_J = Z_{12} + Z_{12,3} J_3 + \frac{1}{2} Z_{12,34} J_3 J_4 + \dots, \quad (5.6.99b)$$

$$\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3 \rangle_J = Z_{123} + Z_{123,4} J_4 + \dots, \quad (5.6.99c)$$

$$\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3, \hat{\mathcal{E}}_4 \rangle_J = Z_{1234} + \dots \quad (5.6.99d)$$

The correlators appearing on the right-hand sides are calculated at fixed fluxes $J_\alpha(\cdot)$. Since $J_\alpha = \dot{B}_\alpha$, fixing the functions $J_\alpha(\cdot)$ is equivalent to fixing $B_\alpha(\cdot)$. Equations (5.6.99) define functions Z_{\dots} . They are simply related to the functions Q_{\dots} . Substituting $J_1 = p_1 B_1$ into (5.6.99) and comparing the resultant equations with (5.6.66), we arrive at

$$\begin{aligned} Z_1 &= Q_1, & Z_{12} &= Q_{12}, & Z_{123} &= Q_{123}, & Z_{1234} &= Q_{1234}, \\ Z_{12,3} &= Q_{12,3} p_3^{-1}, & Z_{123,4} &= Q_{123,4} p_4^{-1}, \\ Z_{12,34} &= Q_{12,34} p_3^{-1} p_4^{-1}, \dots \end{aligned} \quad (5.6.100)$$

By using (5.6.9, 10, 100), FDRs (5.6.74, 86) can be written as

$$Z_{12} = kT \Theta_2^- (Z_{1,2} + Z_{2,1}), \quad (5.6.101a)$$

$$Z_{12,3} = kT [\Theta_2^- Z_{1,23} + \Theta_1^+ Z_{2,13} - (p_1 \Theta_2 + p_2 \Theta_1) p_3^{-1} Z_{3,12}^{t.c.}], \quad (5.6.101b)$$

$$\begin{aligned} Z_{123} &= -(kT)^2 [\Theta_2^- \Theta_3^- (Z_{1,23} + Z_{2,13}^{t.c.}) \\ &\quad + \Theta_1^+ \Theta_3^- (Z_{2,13} + Z_{2,13}^{t.c.}) + \Theta_1^+ \Theta_2^+ (Z_{3,12} + Z_{3,12}^{t.c.})]. \end{aligned} \quad (5.6.101c)$$

Here, as in Sect. 5.3.7, $\Theta^\pm = i\hbar\beta p\Gamma^\pm$, $\Theta = i\hbar\beta p\Gamma$. In the nonquantum limit Θ^\pm and Θ tend to unity, and we obtain the nonquantum relations

$$Z_{12} = kT (Z_{1,2} + Z_{2,1}) \quad (5.6.102a)$$

$$Z_{12,3} = kT (Z_{1,23} + Z_{2,13} + Z_{3,12}^{t.c.}) \quad (5.6.102b)$$

$$Z_{123} = -(kT)^2 P_{123} (Z_{1,23} + Z_{2,13}^{t.c.}). \quad (5.6.102c)$$

The FDRs (5.6.101) have the same structure as the FDRs of the second kind (5.3.92, 95, 97).

5.7 Cubic FDRs of the Third Kind

5.7.1 Relation Between Four-Subscript Functions $L_{...}$ and Functions $G_{...}$

We now proceed to consider the cubic relations of the third kind, i.e. relations connecting the four-subscript functions $Q_{12,34}$, $Q_{123,4}$ and Q_{1234} , which are defined by (5.6.66), with impedance $Q_{1,234}$. For simplifying the calculations we shall assume that the quadratic nonlinearity is equal to zero, i.e. that

$$G_{1,23} = 0. \quad (5.7.1)$$

In this case, instead of (5.2.4) and (5.6.44), we have

$$\begin{aligned} \langle \hat{B}_1 \rangle &= G_{1,2} h_2 + \frac{1}{6} G_{1,234} h_2 h_3 h_4, \\ \langle \hat{B}_1, \hat{B}_2 \rangle &= G_{12} + \frac{1}{2} G_{12,34} h_3 h_4, \\ \langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle &= G_{123,4} h_4, \\ \langle \hat{B}_1, \hat{B}_2, \hat{B}_3, \hat{B}_4 \rangle &= G_{1234}. \end{aligned} \quad (5.7.2)$$

In fact, as a consequence of (5.3.65, 89), equation (5.7.1) implies that the functions $G_{12,3}$ and G_{123} vanish. According to (5.6.11), the equations

$$Q_{1,23} = 0 \quad (5.7.3a)$$

$$Q_{1,234} = -Q_1 Q_2^T Q_3^T Q_4^T G_{1,234} \quad (5.7.3b)$$

follow from (5.7.1) as well. In the approximation (5.6.49), and in the case (5.7.1), equation (5.6.46) takes the form

$$\hat{\mathcal{E}}_1 = -h_1 + Q_{1,2} \hat{B}_2 + \frac{1}{6} Q_{1,234} \hat{B}_2 \hat{B}_3 \hat{B}_4. \quad (5.7.4)$$

We first examine how the functions $L_{...}$ can be expressed in terms of the four-subscript functions $G_{...}$. Using (5.7.4), we can find the correlator $\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2 \rangle$. By analogy with (5.6.50), using the rules given in Sect. 2.1.2, we arrive at

$$\begin{aligned} \langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2 \rangle &= Q_1 Q_2 \langle \hat{B}_1, \hat{B}_2 \rangle + \frac{1}{6} Q_1 Q_{2,567} \langle \hat{B}_1, \hat{B}_5 \hat{B}_6 \hat{B}_7 \rangle \\ &\quad + \frac{1}{6} Q_2 Q_{1,567} \langle \hat{B}_5 \hat{B}_6 \hat{B}_7, \hat{B}_2 \rangle \\ &= Q_1 Q_2 \langle \hat{B}_1, \hat{B}_2 \rangle + \frac{1}{6} Q_1 Q_{2,567} (\langle \hat{B}_1, \hat{B}_5 \rangle \langle \hat{B}_6 \rangle \langle \hat{B}_7 \rangle \\ &\quad + \langle \hat{B}_1, \hat{B}_6 \rangle \langle \hat{B}_5 \rangle \langle \hat{B}_7 \rangle + \langle \hat{B}_1, \hat{B}_7 \rangle \langle \hat{B}_5 \rangle \langle \hat{B}_6 \rangle) \\ &\quad + \frac{1}{6} Q_2 Q_{1,567} (\langle \hat{B}_5, \hat{B}_2 \rangle \langle \hat{B}_6 \rangle \langle \hat{B}_7 \rangle \\ &\quad + \langle \hat{B}_6, \hat{B}_2 \rangle \langle \hat{B}_5 \rangle \langle \hat{B}_7 \rangle + \langle \hat{B}_7, \hat{B}_2 \rangle \langle \hat{B}_5 \rangle \langle \hat{B}_6 \rangle). \end{aligned} \quad (5.7.5)$$

Here the other terms are not written down since they give contributions of higher order in kT (for $\hbar\omega \sim kT$). All three terms in parentheses give an identical result due to the symmetry of the type $Q_{2,567} = Q_{2,657}$, etc. Substituting (5.7.2) into (5.7.5), we obtain the function $L_{12,34}$ defined by (5.6.45b). Namely,

$$L_{12,34} = Q_1 Q_2 G_{12,34} + (Q_1 G_{15} Q_{2,534} + Q_2 G_{52} Q_{1,534}) G_3 G_4. \quad (5.7.6)$$

In order to find $L_{123,4}$, we can write down the triple correlator of random forces

$$\begin{aligned} \langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3 \rangle &= Q_1 Q_2 Q_3 \langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle + \frac{1}{6} Q_1 Q_2 Q_{3,567} \\ &\quad \times \langle \hat{B}_1, \hat{B}_2, \hat{B}_5 \hat{B}_6 \hat{B}_7 \rangle + \frac{1}{6} Q_1 Q_{2,567} Q_3 \\ &\quad \times \langle \hat{B}_1, \hat{B}_5 \hat{B}_6 \hat{B}_7, \hat{B}_3 \rangle \\ &\quad + \frac{1}{6} Q_{1,567} Q_2 Q_3 \langle \hat{B}_5 \hat{B}_6 \hat{B}_7, \hat{B}_2, \hat{B}_3 \rangle \end{aligned} \quad (5.7.7)$$

by using (5.7.4). As a consequence of an equation of the type

$$\begin{aligned} Q_{3,567} \langle \hat{B}_1, \hat{B}_2, \hat{B}_5 \hat{B}_6 \hat{B}_7 \rangle &= 6Q_{3,567} \langle \hat{B}_1, \hat{B}_5 \rangle \\ &\quad \times \langle \hat{B}_2, \hat{B}_6 \rangle \langle \hat{B}_7 \rangle [1 + \mathcal{O}(kT)], \end{aligned} \quad (5.7.8)$$

formula (5.7.7) goes over into

$$\begin{aligned} \langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3 \rangle &= Q_1 Q_2 Q_3 \langle \hat{B}_1, \hat{B}_2, \hat{B}_3 \rangle \\ &\quad + (Q_1 Q_2 \langle \hat{B}_1, \hat{B}_5 \rangle \langle \hat{B}_2, \hat{B}_6 \rangle Q_{3,567} \\ &\quad + Q_1 Q_3 \langle \hat{B}_1, \hat{B}_5 \rangle \langle \hat{B}_6, \hat{B}_3 \rangle Q_{2,567} \\ &\quad + Q_2 Q_3 \langle \hat{B}_5, \hat{B}_2 \rangle \langle \hat{B}_6, \hat{B}_3 \rangle Q_{1,567}) \langle \hat{B}_7 \rangle. \end{aligned} \quad (5.7.9)$$

Here the terms of higher orders than $(kT)^2$ have been omitted. Substituting (5.7.2) into (5.7.9), selecting the terms linear in h , and applying (5.6.45c), we have

$$\begin{aligned} L_{123,4} &= Q_1 Q_2 Q_3 G_{123,4} + (Q_1 Q_2 G_{15} G_{26} Q_{3,564} \\ &\quad + Q_1 Q_3 G_{15} G_{63} Q_{2,564} + Q_2 Q_3 G_{52} G_{63} Q_{1,564}) G_4. \end{aligned} \quad (5.7.10)$$

Finally, we proceed to calculate the quadruple correlator $\langle \hat{\mathcal{E}}_1, \hat{\mathcal{E}}_2, \hat{\mathcal{E}}_3, \hat{\mathcal{E}}_4 \rangle = L_{1234} + \dots$. In doing so we can set $h \equiv 0$. Only terms of order $(kT)^3$ will be of interest. Using (5.7.4), in this approximation we have

$$\begin{aligned} L_{1234} &= Q_1 Q_2 Q_3 Q_4 G_{1234} + \frac{1}{6} Q_1 Q_2 Q_3 Q_{4,567} \langle \hat{B}_1, \hat{B}_2, \hat{B}_3, \hat{B}_5 \hat{B}_6 \hat{B}_7 \rangle \\ &\quad + \frac{1}{6} Q_1 Q_2 Q_{3,567} Q_4 \langle \hat{B}_1, \hat{B}_2, \hat{B}_5 \hat{B}_6 \hat{B}_7, \hat{B}_4 \rangle \\ &\quad + \frac{1}{6} Q_1 Q_{2,567} Q_3 Q_4 \langle \hat{B}_1, \hat{B}_5 \hat{B}_6 \hat{B}_7, \hat{B}_3, \hat{B}_4 \rangle \\ &\quad + \frac{1}{6} Q_{1,567} Q_2 Q_3 Q_4 \langle \hat{B}_5 \hat{B}_6 \hat{B}_7, \hat{B}_2, \hat{B}_3, \hat{B}_4 \rangle. \end{aligned} \quad (5.7.11)$$

In this approximation one can also use equations of the type

$$\begin{aligned} Q_{4,567} \langle \hat{B}_1, \hat{B}_2, \hat{B}_3, \hat{B}_5 \hat{B}_6 \hat{B}_7 \rangle &= 6Q_{4,567} \langle \hat{B}_1, \hat{B}_5 \rangle \langle \hat{B}_2, \hat{B}_6 \rangle \langle \hat{B}_3, \hat{B}_7 \rangle \\ &= 6Q_{4,567} G_{15} G_{26} G_{37}. \end{aligned} \quad (5.7.12)$$

This leads to

$$\begin{aligned} L_{1234} &= Q_1 Q_2 Q_3 Q_4 G_{1234} + Q_1 Q_2 Q_3 G_{15} G_{26} G_{37} Q_{4,567} \\ &\quad + Q_1 Q_2 Q_4 G_{15} G_{26} G_{74} Q_{3,567} + Q_1 Q_3 Q_4 G_{15} G_{63} G_{74} Q_{2,567} \\ &\quad + Q_2 Q_3 Q_4 G_{52} G_{63} G_{74} Q_{1,567}. \end{aligned} \quad (5.7.13)$$

5.7.2 Dissipationally Determinable and Dissipationally Undeterminable Parts of the Functions L_{\dots}

As we have seen in Sect. 5.4, the four-subscript functions G_{1234} , $G_{123,4}$, $G_{12,34}$ are split into dissipationally determinable and dissipationally undeterminable parts. Let us substitute (5.4.45, 28, 16) into (5.7.6, 10, 13), respectively. Then functions $L_{12,34}$, $L_{123,4}$, L_{1234} are also divided into dissipationally determinable and dissipationally undeterminable parts:

$$\begin{aligned} L_{12,34} &= L_{12,34}^{(1)} + L_{12,34}^{(2)}, \\ L_{123,4} &= L_{123,4}^{(1)} + L_{123,4}^{(2)}, \\ L_{1234} &= L_{1234}^{(1)} + L_{1234}^{(2)}. \end{aligned} \quad (5.7.14)$$

Of course, the additional terms in (5.7.6, 10, 13), which do not contain $G_{12,34}$, $G_{123,4}$, G_{1234} and which are expressed in terms of $Q_{1,2}$, $Q_{1,234}$, G_{12} , should be included in the dissipationally determinable parts $L_{12,34}^{(1)}$, $L_{123,4}^{(1)}$, $L_{1234}^{(1)}$. Therefore, we have the following formulas for dissipationally determinable parts:

$$L_{12,34}^{(1)} = Q_1 Q_2 G_{12,34}^{(1)} + (Q_1 G_{15} Q_{2,534} + Q_2 G_{52} Q_{1,534}) G_3 G_4, \quad (5.7.15a)$$

$$\begin{aligned} L_{123,4}^{(1)} &= Q_1 Q_2 Q_3 G_{123,4}^{(1)} + (Q_1 Q_2 G_{15} G_{26} Q_{3,564} + Q_1 Q_3 G_{15} G_{63} Q_{2,564} \\ &\quad + Q_2 Q_3 G_{52} G_{63} Q_{1,564}) G_4, \end{aligned} \quad (5.7.15b)$$

$$\begin{aligned} L_{1234}^{(1)} &= Q_1 Q_2 Q_3 Q_4 G_{1234}^{(1)} + Q_1 Q_2 Q_3 G_{15} G_{26} G_{37} Q_{4,567} \\ &\quad + Q_1 Q_2 Q_4 G_{15} G_{26} G_{74} Q_{3,567} + Q_1 Q_3 Q_4 G_{15} G_{63} G_{74} Q_{2,567} \\ &\quad + Q_2 Q_3 Q_4 G_{52} G_{63} G_{74} Q_{1,567}. \end{aligned} \quad (5.7.16)$$

For dissipationally undeterminable parts we have the simpler formulas

$$L_{12,34}^{(2)} = Q_1 Q_2 G_{12,34}^{(2)}, \quad (5.7.17a)$$

$$L_{123,4}^{(2)} = Q_1 Q_2 Q_3 G_{123,4}^{(2)}, \quad (5.7.17b)$$

$$L_{1234}^{(2)} = Q_1 Q_2 Q_3 Q_4 G_{1234}^{(2)}. \quad (5.7.17c)$$

These formulas will be used later.

5.7.3 Stochastic Representation and Its Consequences

In the linear–cubic approximation the stochastic representation of random forces must be taken in a more complex form than (5.6.64). Namely,

$$\mathcal{E}_1 = \sum_{\sigma} [S_{12}^{(\sigma)} \xi_2^{(\sigma)} + S_{123}^{(\sigma)} \xi_2^{(\sigma)} B_3 + \frac{1}{2} S_{12,34}^{(\sigma)} \xi_2^{(\sigma)} B_3 B_4]. \quad (5.7.18)$$

Here $S_{12,34}^{(\sigma)} = S_{12,43}^{(\sigma)}$, and the term M_1 has been omitted. Using (5.7.18) and regarding $B_a(\cdot)$ as fixed functions, we can find the four-subscript functions Q_{\dots} defined by (5.6.66). Calculating the correlator with the help of (5.7.18) and (5.6.65) and selecting the terms bilinear with respect to B , we obtain

$$Q_{12,34} = \sum_{\sigma} [S_{15,34}^{(\sigma)} R_{52}^{(\sigma)} + S_{25,34}^{(\sigma)} R_{15}^{(\sigma)} + P_{34}(S_{153}^{(\sigma)} S_{264}^{(\sigma)} R_{56}^{(\sigma)})]. \quad (5.7.19)$$

Here and subsequently it is supposed that $S_{12}^{(\sigma)} = \delta_{12}$. Even without this supposition all the calculations remain valid, but some formulas become somewhat longer. Introducing the notation

$$J_{1234}^- = \sum_{\sigma} S_{15,34}^{(\sigma)} R_{52}^{(\sigma)}, \quad J_{1234}^+ = \sum_{\sigma} S_{1534}^{(\sigma)} R_{25}^{(\sigma)}, \quad (5.7.20a)$$

$$K_{1234} = \sum_{\sigma} S_{153}^{(\sigma)} S_{264}^{(\sigma)} R_{56}^{(\sigma)}, \quad (5.7.20b)$$

we arrive at

$$Q_{12,34} = J_{1234}^- + J_{2134}^+ + K_{1234} + K_{1243}. \quad (5.7.21)$$

Further, using (5.7.18) for calculating the correlators $\langle \mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3 \rangle_B = Q_{123,4} B_4$ and $\langle \mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3, \mathcal{E}_4 \rangle_B = Q_{1234}$, we obtain

$$Q_{123,4} = \sum_{\sigma} (S_{154}^{(\sigma)} R_{523}^{(\sigma)} + S_{254}^{(\sigma)} R_{153}^{(\sigma)} + S_{354}^{(\sigma)} R_{125}^{(\sigma)}), \quad (5.7.22a)$$

$$Q_{1234} = \sum_{\sigma} R_{1234}^{(\sigma)}. \quad (5.7.22b)$$

It is also useful to introduce the notation

$$\begin{aligned} Q_{123,4}^- &= \sum_{\sigma} S_{154}^{(\sigma)} R_{523}^{(\sigma)}, \\ Q_{123,4}^+ &= \sum_{\sigma} S_{154}^{(\sigma)} R_{253}^{(\sigma)}, \\ Q_{123,4}^{++} &= \sum_{\sigma} S_{154}^{(\sigma)} R_{235}^{(\sigma)}. \end{aligned} \quad (5.7.23)$$

By using (5.7.23), (5.7.22a) takes the form

$$Q_{123,4} = Q_{123,4}^- + Q_{213,4}^+ + Q_{312,4}^{++}. \quad (5.7.24)$$

Let us now assume that the functions $B_a(t)$ are dependent, namely, they are connected with \mathcal{E}_1 by the equation

$$B_1 = G_{1,2}(h_2 + \mathcal{E}_2) + \frac{1}{6} G_{1,234}(h_2 + \mathcal{E}_2)(h_3 + \mathcal{E}_3)(h_4 + \mathcal{E}_4), \quad (5.7.25)$$

which is equivalent to (5.7.4). Substitution of (5.7.25) into (5.7.18) gives

$$\begin{aligned} \mathcal{E}_1 &= \sum_{\sigma} [\xi_1^{(\sigma)} + S_{123}^{(\sigma)} \xi_2^{(\sigma)} G_3(h_3 + \mathcal{E}_3) \\ &\quad + \frac{1}{2} S_{12,34}^{(\sigma)} \xi_2^{(\sigma)} G_3 G_4(h_3 + \mathcal{E}_3)(h_4 + \mathcal{E}_4) + \dots]. \end{aligned} \quad (5.7.26)$$

By iterations the right-hand side of (5.7.26) can be expressed in terms of h_1 and $\xi_1^{(\sigma)}$. To the desired accuracy we have

$$\begin{aligned} \mathcal{E}_1 &= \sigma_1 + \sum_{\sigma} [S_{123}^{(\sigma)} \xi_2^{(\sigma)} G_3(h_3 + \sigma_3) + \sum_{\tau} S_{123}^{(\sigma)} \xi_2^{(\sigma)} G_3 S_{345}^{(\tau)} \xi_4^{(\tau)} G_5(h_5 + \sigma_5) \\ &\quad + \frac{1}{2} S_{12,34}^{(\sigma)} \xi_2^{(\sigma)} G_3 G_4(h_3 + \sigma_3)(h_4 + \sigma_4)], \end{aligned} \quad (5.7.27)$$

where we have denoted for short $\sigma_1 = \sum_{\tau} \xi_1^{(\tau)}$. Terms of third and higher orders in h and of fourth and higher orders in ξ have been omitted. Using (5.7.27) and (5.6.65), one can calculate the correlators $\langle \mathcal{E}_1, \mathcal{E}_2 \rangle$, $\langle \mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3 \rangle$, $\langle \mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3, \mathcal{E}_4 \rangle$ and

thereby find the four-subscript functions L_{\dots} appearing in (5.6.45), i.e. one can express them in terms of Q_{\dots} . Note that one should find $L_{12,34}$, $L_{123,4}$ and L_{1234} retaining only the terms of orders kT , $(kT)^2$ and $(kT)^3$, respectively. The sums of the type (5.6.77) and the sum $\Sigma_\sigma R_{123}^{(\sigma)}$ vanish by virtue of (5.7.1) and (5.6.85). Therefore the terms entering into (5.7.27) and containing $S_{123}S_{345}$ have no influence on the functions L_{\dots} in this approximation.

In order to calculate $L_{12,34}$, it is sufficient to take only the terms linear in ξ in (5.7.27). Using (5.7.19), we get

$$L_{12,34} = Q_{12,34} G_3 G_4 . \quad (5.7.28)$$

For calculating $L_{123,4}$, we omit the terms that are quadratic in h and cubic in ξ in (5.7.27). By using (5.7.20–22) and equation $\Sigma_\sigma R_{12}^{(\sigma)} = Q_{12}$, we find

$$\begin{aligned} L_{123,4} = & (Q_{123,4} + Q_{12,54} G_5 Q_{53} + Q_{13,54}^- G_5 Q_{52} \\ & + Q_{31,54}^+ G_5 Q_{25} + Q_{23,54} G_5 Q_{15}) G_4 , \end{aligned} \quad (5.7.29)$$

where

$$Q_{12,34}^- = J_{1234}^- + K_{1234}, \quad Q_{12,34}^+ = J_{1234}^+ + K_{2143} , \quad (5.7.30)$$

so that

$$Q_{12,34} = Q_{12,34}^- + Q_{21,34}^+ .$$

Finally, in order to calculate $\langle \mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3, \mathcal{E}_4 \rangle = L_{1234}$ one should set $h \equiv 0$ in (5.7.27). Carrying out the calculations, which are omitted, and using (5.7.20–24), we have

$$\begin{aligned} L_{1234} = & Q_{1234} + Q_{123,5} G_5 Q_{54} + (Q_{124,5}^- + Q_{214,5}^+) G_5 Q_{53} + Q_{412,5}^{++} G_5 Q_{35} \\ & + Q_{134,5}^- G_5 Q_{52} + (Q_{314,5}^+ + Q_{413,5}^{++}) G_5 Q_{25} + Q_{234,5} G_5 Q_{15} \\ & + Q_{12,56} G_5 Q_{53} G_6 Q_{64} + (Q_{13,56}^- G_5 Q_{52} + Q_{31,56}^+ G_5 Q_{25}) G_6 Q_{64} \\ & + J_{1456}^- G_5 Q_{52} G_6 Q_{63} + J_{4156}^+ G_5 Q_{25} G_6 Q_{36} \\ & + K_{1456} G_5 Q_{52} G_6 Q_{36} + K_{1465} G_5 Q_{25} G_6 Q_{63} + Q_{23,56} G_5 Q_{15} G_6 Q_{64} \\ & + (Q_{24,56}^- G_5 Q_{53} + Q_{42,56}^+ G_5 Q_{35}) G_6 Q_{16} + Q_{34,56} G_5 Q_{15} G_6 Q_{26} . \end{aligned} \quad (5.7.31)$$

5.7.4 Relations for the Dissipationally Determinable Parts of the Functions Q_{\dots}

According to (5.7.14), the four-subscript functions L_{\dots} are represented in the form of a sum of two parts $L_{\dots}^{(1)}$ and $L_{\dots}^{(2)}$. Likewise the functions $Q_{12,34}$, J_{1234}^\pm , K_{1234} , $Q_{12,34}^\pm$, $Q_{123,4}$, $Q_{123,4}^{\pm\pm}$, Q_{1234} are represented in the same form

$$Q = Q^{(1)} + Q^{(2)} \quad (5.7.32)$$

etc. We demand that (5.7.21, 24, 30, 31) be separately valid for the summands denoted by superscript (1) as well as for those denoted by superscript (2). We define

functions $Q_{12,34}^{(1)}, Q_{123,4}^{(1)}, Q_{1234}^{(1)}$ such that they are related to $L_{12,34}^{(1)}, L_{123,4}^{(1)}, L_{1234}^{(1)}$ by the same equations (5.7.28, 29, 31), through which $Q_{12,34}, Q_{123,4}, Q_{1234}$ are related to $L_{12,34}, L_{123,4}, L_{1234}$. Hence identical equations are valid for functions with the superscript (2). Thus, we have

$$L_{12,34}^{(j)} = Q_{12,34}^{(j)} G_3 G_4, \quad (5.7.33a)$$

$$\begin{aligned} L_{123,4}^{(j)} &= (Q_{123,4}^{(j)} + Q_{12,54}^{(j)} G_5 Q_{53} + Q_{13,54}^{-1(j)} G_5 Q_{52} \\ &\quad + Q_{31,54}^{(j)} G_5 Q_{25} + Q_{23,54}^{(j)} G_5 Q_{15}) G_4, \quad j = 1, 2. \end{aligned} \quad (5.7.33b)$$

We can obtain equations for $L_{1234}^{(j)}$ from (5.7.31) analogously.

On equating (5.7.15a) and (5.7.33a) for $j = 1$ we obtain

$$Q_{12,34}^{(1)} = Q_1 Q_2 Q_3^T Q_4^T G_{12,34}^{(1)} + Q_1 G_{15} Q_{2,534} + Q_2 G_{52} Q_{1,534}. \quad (5.7.34)$$

Substituting (5.4.48) and (5.3.6) into (5.7.34) and also using (5.7.3b), or, more precisely,

$$G_{1,234} = -G_1 G_2^T G_3^T G_4^T Q_{1,234}, \quad (5.7.35)$$

we obtain

$$Q_{12,34}^{(1)} = -i\hbar(\Gamma_2^- Q_{1,234} + \Gamma_1^+ Q_{2,134}). \quad (5.7.36)$$

We see that $Q_{12,34}^{(1)}$ is expressed in terms of the cubic impedance $Q_{1,234}$ and therefore it is the dissipationally determinable part of the function $Q_{12,34}$.

Analogously, equating the expressions in (5.7.33b) for $j = 1$ and in (5.7.15b), one can find $Q_{123,4}^{(1)}$. Substituting (5.4.32) into the expression obtained for $Q_{123,4}^{(1)}$ and using the equation $G_{1,234}^{t.c.} = G_1^{t.c.} G_2 G_3 G_4 Q_{1,234}$ together with (5.7.35, 36), we get after cancellations

$$\begin{aligned} Q_{123,4}^{(1)} &= \hbar^2 [\Gamma_2^- \Gamma_3^- Q_{1,234} + \Gamma_1^+ \Gamma_3^- Q_{2,134} + \Gamma_1^+ \Gamma_2^+ Q_{3,124} \\ &\quad + (\Gamma_2^- \Gamma_3^- + \Gamma_1^+ \Gamma_3^- + \Gamma_1^+ \Gamma_2^+) Q_{4,123}^{t.c.}], \end{aligned} \quad (5.7.37)$$

if we set

$$Q_{12,34}^{\pm(1)} = -i\hbar \Gamma_2^\pm Q_{1,234}. \quad (5.7.38)$$

In the case where (5.7.38) does not hold, the “strange” operator (5.6.63) appears in (5.7.37).

Finally, we use equation (5.7.31), which is written for four-subscript functions carrying the superscript (1). Equating the expression on the right-hand side of (5.7.31) to that in (5.7.16), we can calculate $Q_{1234}^{(1)}$. Here one uses (5.4.20), relations (5.7.36–38) and formula (5.2.105). After numerous cancellations we find

$$\begin{aligned} Q_{1234}^{(1)} &= i\hbar^3 [\Gamma_2^- \Gamma_3^- \Gamma_4^- (Q_{1,234} - Q_{1,234}^{t.c.}) + \Gamma_1^+ \Gamma_3^- \Gamma_4^- (Q_{2,134} - Q_{2,134}^{t.c.}) \\ &\quad + \Gamma_1^+ \Gamma_2^+ \Gamma_4^- (Q_{3,124} - Q_{3,124}^{t.c.}) + \Gamma_1^+ \Gamma_2^+ \Gamma_3^+ (Q_{4,123} - Q_{4,123}^{t.c.})] \end{aligned} \quad (5.7.39)$$

if we set

$$K_{1234}^{(1)} = 0, \quad (5.7.40)$$

$$Q_{123,4}^{\gamma\pm(1)} = \hbar^2 \Gamma_2^\gamma \Gamma_3^\pm (Q_{1,234} + Q_{4,123}^{t.c.}), \quad \gamma = \pm. \quad (5.7.41)$$

Formulas (5.7.36, 37, 39) resemble (5.4.48, 32, 20), respectively. Note that in the nonquantum case we have no need to introduce the functions (5.7.20, 23) or to postulate equations (5.7.38, 40, 41) in order to obtain the final relations.

5.7.5 Relationships for the Dissipationally Undeterminable Parts of the Functions Q_{\dots}

Using (5.7.33a) for $j = 2$ and (5.7.17a), we find

$$Q_{12,34}^{(2)} = Q_1 Q_2 G_{12,34}^{(2)} Q_3 Q_4 = Q_1 Q_2 Q_3^T Q_4^T G_{12,34}^{(2)}. \quad (5.7.42)$$

If we substitute the inverse equation

$$G_{12,34}^{(2)} = G_1 G_2 G_3^T G_4^T Q_{12,34}^{(2)} \quad (5.7.43)$$

into (5.4.59, 61), we obtain the relations

$$Q_{12,34}^{(2)} = Q_{21,34}^{(2)}, \quad \Gamma_3^- \Gamma_4^- Q_{12,34}^{(2)\text{t.c.}} = \Gamma_1^+ \Gamma_2^+ Q_{34,12}^{(2)}, \quad (5.7.44)$$

which have the same form as (5.4.59, 61).

Let us now consider equations (5.7.33b) for $j = 2$ and (5.7.17b). Excluding $L_{123,4}^{(2)}$ gives

$$\begin{aligned} Q_{123,4}^{(2)} &= Q_1 Q_2 Q_3 Q_4^T G_{123,4}^{(2)} - i\hbar(X_3 - 1) \Gamma_3^- Q_{12,34}^{(2)} - i\hbar(X_2 - 1) \\ &\quad \times (\Gamma_2^- Q_{13,24}^{(2)} + \Gamma_2^+ Q_{31,24}^{(2)}) - i\hbar(X_1 - 1) \Gamma_1^+ Q_{23,14}^{(2)}. \end{aligned} \quad (5.7.45)$$

Here the formulas $Q_{12} = L_{12} = -i\hbar\Gamma_2^-(Q_{1,2} - Q_{2,1})$ and $G_1 Q_{12} = -i\hbar\Gamma_2^-(1 - X_1^T)$ have been used. However, as a consequence of (5.4.70) and (5.7.43) we have

$$\begin{aligned} Q_1 Q_2 Q_3 Q_4^T G_{123,4}^{(2)} &= i\hbar(X_3 \Gamma_3^- Q_{12,34}^{(2)} + X_1 \Gamma_1^+ Q_{23,14}^{(2)}) \\ &\quad + i\hbar X_2 Q_1 Q_2 Q_3 Q_4^T (\Gamma_2^- G_{13,24}^{(2)} + \Gamma_2^+ G_{31,24}^{(2)}). \end{aligned} \quad (5.7.46)$$

Let us substitute (5.7.46) into (5.7.45). On doing this the terms with X_1 and X_3 cancel out. A necessary and sufficient condition for the terms containing X_2 to drop out is the equation

$$Q_{12,34}^{(2)} = Q_1 Q_2 G_{12,34}^{(2)} Q_3 Q_4 \quad (5.7.47a)$$

or

$$Q_{21,34}^{(2)} = Q_1 Q_2 G_{21,34}^{(2)} Q_3 Q_4. \quad (5.7.47b)$$

Using (5.7.47), from (5.7.45, 46) we obtain after cancellations:

$$Q_{123,4}^{(2)} = i\hbar(\Gamma_3^- Q_{12,34}^{(2)} + \Gamma_2^- Q_{13,24}^{(2)} + \Gamma_2^+ Q_{31,24}^{(2)} + \Gamma_1^+ Q_{23,14}^{(2)}). \quad (5.7.48)$$

Finally, we use (5.7.17c) and formula (5.7.31), which is written for the dissipationally undeterminable part of the four-subscript functions. Here one should also use (5.4.78) and (5.7.3b, 43, 47, 48). If we set

$$J_{1234}^{\pm(2)} = Q_1 Q_2 C_{1234}^{\pm} Q_3 Q_4, \quad (5.7.49)$$

$$K_{1234}^{(2)} = Q_1 Q_2 D_{1234} Q_3 Q_4$$

and

$$\begin{aligned} Q_{123,4}^{--(2)} &= i\hbar(\Gamma_3^- Q_{12,43}^{-(2)} + \Gamma_2^- J_{1342}^{-(2)} + \Gamma_2^+ K_{1342}^{(2)}) , \\ Q_{123,4}^{+- (2)} &= i\hbar(\Gamma_3^- Q_{12,43}^{+(2)} + \Gamma_2^+ Q_{13,42}^{-(2)}) , \\ Q_{123,4}^{++(2)} &= i\hbar(\Gamma_3^+ J_{1243}^{+(2)} + \Gamma_3^- K_{2134}^{(2)} + \Gamma_2^+ Q_{13,42}^{+(2)}) , \end{aligned} \quad (5.7.50)$$

all the terms containing the “strange” operators X_k cancel out, and we arrive at

$$\begin{aligned} Q_{1234}^{(2)} = -\hbar^2 &[\Gamma_3^- \Gamma_4^- Q_{12,34}^{(2)} + \Gamma_4^- (\Gamma_2^- Q_{13,24}^{-(2)} + \Gamma_2^+ Q_{31,24}^{+(2)}) \\ &+ \Gamma_2^- \Gamma_3^- J_{1423}^{-(2)} + \Gamma_2^+ \Gamma_3^+ J_{4123}^{+(2)} + \Gamma_2^- \Gamma_3^+ K_{1423}^{(2)} + \Gamma_2^+ \Gamma_3^- K_{1432}^{(2)} \\ &+ \Gamma_1^+ \Gamma_4^- Q_{23,14}^{(2)} + \Gamma_1^+ (\Gamma_3^- Q_{24,31}^{-(2)} + \Gamma_3^+ Q_{42,31}^{+(2)}) + \Gamma_1^+ \Gamma_2^+ Q_{34,12}^{(2)}] . \end{aligned} \quad (5.7.51)$$

Using (5.7.49) and (5.4.76), we easily get the equations

$$\begin{aligned} \hbar^2 J_{12,34}^{\pm(2)} &= \Gamma_2^\pm \tilde{M}_{1234} , \\ \hbar^2 K_{1234}^{(2)} &= \Gamma_{24}^- \tilde{N}_{1234} , \end{aligned} \quad (5.7.52)$$

which are analogous to (5.4.76). Here we have used the notation

$$\begin{aligned} \tilde{M}_{1234} &= Q_1 Q_2 M_{1234} Q_3 Q_4 , \\ \tilde{N}_{1234} &= Q_1 Q_2 N_{1234} Q_3 Q_4 . \end{aligned} \quad (5.7.53)$$

Formula (5.7.53) implies that the functions $\tilde{M}_{1234}, \tilde{N}_{1234}$ have the same properties (5.4.53) as M_{1234}, N_{1234} . From (5.7.51) we can therefore derive the relation

$$\begin{aligned} Q_{1234}^{(2)} = -\hbar^2 &[\Gamma_3^- \Gamma_4^- Q_{12,34}^{(2)} + \Gamma_4^- (\Gamma_2^- Q_{13,24}^{-(2)} + \Gamma_2^+ Q_{31,24}^{+(2)}) \\ &+ E_1 \Gamma_2^+ \Gamma_3^+ Q_{41,23}^{(2)} + \Gamma_1^+ \Gamma_4^- Q_{23,14}^{(2)} \\ &+ \Gamma_1^+ (\Gamma_3^- Q_{24,31}^{-(2)} + \Gamma_3^+ Q_{42,31}^{+(2)}) + \Gamma_1^+ \Gamma_2^+ Q_{34,12}^{(2)}] \end{aligned} \quad (5.7.54)$$

and other relations by the same method as formula (5.4.85) and the others have been obtained from (5.4.78).

Thus, the relations that are valid for the functions $G_{\dots}^{(2)}$ are also valid for the functions $Q_{\dots}^{(2)}$.

5.7.6 Another Form of Cubic FDRs of the Third Kind

From the relations derived above we can easily obtain the relations connecting the four-subscript functions Z_{\dots} [which are defined by (5.6.99, 100)] with modified impedances $Z_{1,234}$ (cf. (5.6.10)). From (5.7.36, 37, 39) we obtain relations for the dissipationally determinable parts

$$Z_{12,34}^{(1)} = kT(\Theta_2^- Z_{1,234} + \Theta_1^+ Z_{2,134}) , \quad (5.7.55a)$$

$$\begin{aligned} Z_{123,4}^{(1)} = - (kT)^2 &[\Theta_2^- \Theta_3^- Z_{1,234} + \Theta_1^+ \Theta_3^- Z_{2,134} + \Theta_1^+ \Theta_2^+ Z_{3,124} \\ &- (p_1 \Theta_2^- \Theta_3^- + p_2 \Theta_1^+ \Theta_3^- + p_3 \Theta_1^+ \Theta_2^+) p_4^{-1} Z_{4,123}^{t.c.}] , \end{aligned} \quad (5.7.55b)$$

$$\begin{aligned} Z_{1234}^{(1)} = & (kT)^3 [\Theta_2^- \Theta_3^- \Theta_4^- (Z_{1,234} + Z_{1,234}^{\text{t.c.}}) \\ & + \Theta_1^+ \Theta_3^- \Theta_4^- (Z_{2,134} + Z_{2,134}^{\text{t.c.}}) + \Theta_1^+ \Theta_2^+ \Theta_4^- (Z_{3,124} + Z_{3,124}^{\text{t.c.}}) \\ & + \Theta_1^+ \Theta_2^+ \Theta_3^+ (Z_{4,123} + Z_{4,123}^{\text{t.c.}})] , \end{aligned} \quad (5.7.55\text{c})$$

where $\Theta^\pm(p) = i\hbar\beta p\Gamma^\pm(p)$. From (5.7.44, 48, 54) we find relations for the dissipationally undeterminable parts

$$Z_{12,34}^{(2)} = Z_{21,34}^{(2)}, \quad (5.7.56\text{a})$$

$$\Theta_3^- \Theta_4^- Z_{12,34}^{(2)\text{t.c.}} = \Theta_1^+ \Theta_2^+ Z_{34,12}^{(2)}, \quad (5.7.56\text{b})$$

$$\begin{aligned} Z_{123,4}^{(2)} = & -kT(\Theta_3^- Z_{12,34}^{(2)} + \Theta_2^- Z_{13,24}^{(2)} \\ & + \Theta_2^+ Z_{31,24}^{(2)} + \Theta_1^+ Z_{23,14}^{(2)}) , \end{aligned} \quad (5.7.56\text{c})$$

$$\begin{aligned} Z_{1234}^{(2)} = & (kT)^2 [\Theta_3^- \Theta_4^- Z_{12,34}^{(2)} + \Theta_4^- (\Theta_2^- Z_{13,24}^{(2)} + \Theta_2^+ Z_{31,24}^{(2)}) \\ & + E_1 \Theta_2^+ \Theta_3^+ Z_{14,23}^{(2)} + \Theta_1^+ \Theta_4^- Z_{23,14}^{(2)} \\ & + \Theta_1^+ (\Theta_3^- Z_{24,31}^{(2)} + \Theta_3^+ Z_{42,31}^{(2)}) + \Theta_1^+ \Theta_2^+ Z_{34,12}^{(2)}] . \end{aligned} \quad (5.7.56\text{d})$$

Moreover, we have $Z_{12,34}^{-(2)} + Z_{21,34}^{+(2)} = Z_{12,34}^{(2)}$ and $Z_{12,34}^{\pm(2)} = Q_{12,34}^{\pm(2)} p_3^{-1} p_4^{-1}$. In the nonquantum limit there is no need to split the function $Z_{12,34}^{(2)}$ into two parts $Z_{12,34}^{\pm(2)}$, and instead of (5.7.55c,d) we get

$$\begin{aligned} Z_{123,4}^{(2)} = & -kTP_{(123)} Z_{12,34}^{(2)}, \\ Z_{1234}^{(2)} = & (kT)^2 (Z_{12,34}^{(2)} + Z_{13,24}^{(2)} + Z_{14,23}^{(2)} + Z_{23,14}^{(2)} + Z_{24,31}^{(2)} + Z_{34,12}^{(2)}) . \end{aligned} \quad (5.7.57)$$

Instead of (5.7.18) the modified stochastic representation

$$\mathcal{E}_1 = M_1 + \sum_\sigma (T_{12}^{(\sigma)} \xi_2^{(\sigma)} + T_{123}^{(\sigma)} \xi_2^{(\sigma)} J_3 + \frac{1}{2} T_{12,34}^{(\sigma)} \xi_2^{(\sigma)} J_3 J_4) , \quad (5.7.58)$$

corresponds to the above modified relations. Here

$$T_{123}^{(\sigma)} p_3 = S_{123}^{(\sigma)}, \quad T_{12,34}^{(\sigma)} p_3 p_4 = S_{12,34}^{(\sigma)}, \quad T_{12}^{(\sigma)} = S_{12}^{(\sigma)} . \quad (5.7.59)$$

Using (5.7.58) instead of (5.7.18) and also relations from Sects. 5.3.7 and 5.4.9 and applying analogous methods, we can immediately derive the FDRs for $Z_{12}, Z_{12,3}, Z_{123}, Z_{12,34}, Z_{123,4}, Z_{1234}$ instead of the FDRs of Sects. 5.7.4, 5.

5.8 Notes on References to Chapter 5

Linear non-Markov nonequilibrium thermodynamics relations are considered in many monographs, for example in [5.11]. These relations have numerous applications.

The nonlinear FDRs of the first kind are first considered here. Both of the quadratic FDRs of the second kind were obtained in [5.8]. In [5.7] another form of writing the most important of these FDRs was suggested and the method of its derivation was simplified. In the same work it was proved that the cubic theory had

no analogous formula, i.e. the formula by which the four-subscript (quadruple) moment was expressed in terms of cubic admittance.

A number of new cubic FDRs of the second kind have been obtained in this chapter. Nonlinear FDRs of the third kind were derived in [5.12, 13]. In Sects. 5.6, 7 the method of [5.12, 13], i.e. the application of stochastic representation of fluctuating forces, has been used.

6. Some Uses of Non-Markov FDRs

This chapter considers the uses of the fluctuation–dissipation relations (derived in the previous chapter) in some relatively simple cases, mostly when the internal parameters form a Markov process. For such cases it is possible to compute the many-time admittances $Y_{1,2}$, $Y_{1,23}$, $Y_{1,234}$, namely to express them through the time-independent matrices $d_{\alpha\beta}$, $f_{\alpha\beta\gamma}$, and $f_{\alpha\beta\gamma\delta}$, which enter into the inertialess relaxation equation

$$\dot{A}_\alpha = -d_{\alpha\beta} A_\beta + \frac{1}{2} f_{\alpha\beta\gamma} A_\beta A_\gamma + \frac{1}{6} f_{\alpha\beta\gamma\delta} A_\beta A_\gamma A_\delta .$$

An advantage of Markov cases over non-Markov cases is that the dissipationally undeterminable multitime function $Y_{12,34}^{(2)}$ can be expressed in terms of the time-independent matrix $c_{\alpha\beta,\gamma\delta}$, which incidentally is often expressed through only one or two dissipationally undeterminable parameters. This sharply decreases the degree of uncertainty that remains after the dissipational properties of a system are known.

It is also shown how FDRs of the third kind enable one to find correlators of internal parameters and their derivatives in the case when a composite system has dissipative elements with different temperatures. The chapter goes on to show that these FDRs in particular enable one to calculate such a specific effect as the emergence of relatively weak fluxes, which result from uncompensated detection of fluctuations in quadratic dissipative elements having different temperatures.

6.1 Calculation of Many-Time Equilibrium Correlators and Their Derivatives in the Markov Case

6.1.1 Linear and Quadratic Admittances in the Markov Case

In Sects. 4.3, 5 we discussed techniques of computation of the approximate operator of the master equation from the relaxation equation in the Markov case. Solving the master equation enables one in principle to work out two, three and fourfold many-time correlators, both equilibrium and nonequilibrium, under various initial conditions. However, the many-time equilibrium correlators or corresponding spectral densities can be calculated in a simpler and unified way in terms of non-Markov FDRs, which are of course also applicable to the Markov case. Using relaxation equations, for example, it is possible to find admittances and from them

obtain the correlators using the non-Markov FDRs of the second kind (Sects. 5.3, 4). We will now use this technique to obtain twofold and threefold correlators.

The standard form of the phenomenological relaxation equations in the linear-quadratic approximation is

$$\dot{A}_\alpha = l_{\alpha, \beta} x_\beta + \frac{1}{2} l_{\alpha, \beta\gamma} x_\beta x_\gamma , \quad (6.1.1)$$

where $x_\beta = \partial F(A)/\partial A_\beta$. In a given approximation we may use the free energy in the form

$$F(A) = \frac{1}{2} r_{\alpha\beta}^{-1} A_\alpha A_\beta + \frac{1}{6} s_{\alpha\beta\gamma} A_\alpha A_\beta A_\gamma + \text{const.} \quad (6.1.2)$$

(we here put $A^0 = 0$, i.e. the origin of the coordinates is placed at the equilibrium point A^0).

It was shown in Sect. 5.5 that the hypothesis of the simplest inclusion of external forces (5.5.8) leads to complete agreement of FDRs of the second kind with FDRs of the first kind and hence with Markov FDRs. Applying the hypothesis to (6.1.1) gives

$$\dot{A}_\alpha = l_{\alpha, \beta} (x_\beta - h_\beta) + \frac{1}{2} l_{\alpha, \beta\gamma} (x_\beta - h_\beta)(x_\gamma - h_\gamma) . \quad (6.1.3)$$

Substituting into (6.1.3) the expression $x_\beta = r_{\beta\gamma}^{-1} A_\gamma + \frac{1}{2} s_{\beta\gamma\delta} A_\gamma A_\delta$, which can be derived from (6.1.2), we obtain

$$\begin{aligned} \dot{A}_\alpha + d_{\alpha\gamma} A_\gamma &= -l_{\alpha, \beta} h_\beta + \frac{1}{2} (l_{\alpha, \beta} s_{\beta\rho\sigma} + l_{\alpha, \beta\gamma} r_{\beta\rho}^{-1} r_{\gamma\sigma}^{-1}) A_\rho A_\sigma \\ &\quad + \frac{1}{2} l_{\alpha, \beta\gamma} (-2r_{\beta\rho}^{-1} A_\rho h_\gamma + h_\beta h_\gamma) , \end{aligned} \quad (6.1.4)$$

where

$$d_{\alpha\gamma} = -l_{\alpha, \beta} r_{\beta\gamma}^{-1} . \quad (6.1.5)$$

In (6.1.4) we have only kept the terms linear and quadratic in A , since the higher terms exert no influence on the admittances $G_{1,2}$ and $G_{1,23}$, which are of interest to us. The linear admittance $G_{1,2}$ can readily be found from (6.1.4) if the latter is stripped of all the nonlinear terms. Integrating the equation $\dot{A}_\alpha + d_{\alpha\gamma} A_\gamma = -l_{\alpha, \beta} h_\beta$, we have

$$A_\alpha(t_1) = \int G_{\alpha\beta}(t_{12}) h_\beta(t_2) dt_2 , \quad (6.1.6a)$$

$$G_{\alpha\beta}(t_{12}) = -V_{\alpha\gamma}(t_{12}) l_{\gamma, \beta} , \quad (6.1.6b)$$

where

$$V_{\alpha\gamma}(t) = [\exp(-\hat{D}t)]_{\alpha\gamma} \vartheta(t), \quad \hat{D} = \|d_{\alpha\gamma}\| . \quad (6.1.7)$$

The quadratic admittance $G_{1,23}$ can be derived from (6.1.4) by solving the above equation following the scheme

$$\begin{aligned} \dot{A}_\alpha + d_{\alpha\gamma} A_\gamma &= -l_{\alpha, \beta} h_\beta + \frac{1}{2} (l_{\alpha, \beta} s_{\beta\rho\sigma} + l_{\alpha, \beta\gamma} r_{\beta\rho}^{-1} r_{\gamma\sigma}^{-1}) A_\rho^{(1)} A_\sigma^{(1)} \\ &\quad + \frac{1}{2} l_{\alpha, \beta\gamma} (-2r_{\beta\rho}^{-1} A_\rho^{(1)} + h_\beta) h_\gamma , \end{aligned} \quad (6.1.8)$$

where $A_1^{(1)} = G_{1,2} h_2$ is a solution in a linear approximation. From (6.1.8) we get

$A_1 = G_{1,2}h_2 + G_{1,23}h_2h_3/2$, where

$$G_{1,23}h_2h_3 = \int V_{\alpha_1,\tau}(t_{10}) \{ (l_{\tau,\beta} s_{\beta\rho\sigma} + l_{\tau,\beta\gamma} r_{\beta\rho}^{-1} r_{\gamma\sigma}^{-1}) A_\rho^{(1)}(t_0) A_\sigma^{(1)}(t_0) \\ + l_{\tau,\beta\gamma} [-2r_{\beta\rho}^{-1} A_\rho^{(1)}(t_0) + h_\beta(t_0)] h_\gamma(t_0) \} dt_0, \quad (6.1.9)$$

i.e.

$$G_{\mu,v\lambda}(t_1, t_2, t_3) = \int dt_0 V_{\mu\tau}(t_{10}) (l_{\tau,\beta} s_{\beta\rho\sigma} + l_{\tau,\beta\gamma} r_{\beta\rho}^{-1} r_{\gamma\sigma}^{-1}) G_{\rho v}(t_{02}) G_{\sigma\lambda}(t_{03}) \\ - V_{\mu\tau}(t_{12}) l_{\tau,v\gamma} r_{\gamma\rho}^{-1} G_{\rho\lambda}(t_{23}) - V_{\mu\tau}(t_{13}) l_{\tau,\beta\lambda} r_{\beta\rho}^{-1} G_{\rho v}(t_{32}) \\ + V_{\mu\tau}(t_{12}) l_{\tau,v\lambda} \delta(t_{23}). \quad (6.1.10)$$

Integration with respect to t_0 here is actually between $t_m = \max(t_2, t_3)$ and t_1 .

The admittances (6.1.6) and (6.1.10) can easily be reduced to the spectral representation given by (5.2.14). Taking the Fourier integral of (6.1.6b),

$$-(2\pi)^{-1} \int \exp(-i\omega_1 t_1 - i\omega_2 t_2) V_{\alpha\gamma}(t_{12}) l_{\gamma,\beta} dt_1 dt_2 \quad (6.1.11)$$

and using (6.1.7), we readily find

$$G_{\alpha,\beta}(\omega_1, \omega_2) = -(i\omega_1 \hat{I} + \hat{D})_{\alpha\gamma}^{-1} l_{\gamma,\beta} \delta(\omega_1 + \omega_2). \quad (6.1.12)$$

Here

$$\int \exp(-i\omega t) V_{\alpha\gamma}(t) dt = (i\omega \hat{I} + \hat{D})_{\alpha\gamma}^{-1} \equiv (i\omega + \hat{D})_{\alpha\gamma}^{-1}. \quad (6.1.13)$$

Computation of the integral (5.2.14) of (6.1.10) using (6.1.12, 13) gives

$$G_{\mu,v\lambda}(\omega_1, \omega_2, \omega_3) \\ = (2\pi)^{-1/2} (i\omega_1 + \hat{D})_{\mu\tau}^{-1} \{ (l_{\tau,\beta} s_{\beta\rho\sigma} + l_{\tau,\beta\gamma} r_{\beta\rho}^{-1} r_{\gamma\sigma}^{-1}) [(-i\omega_2 + \hat{D})^{-1} \hat{L}]_{\rho v} \\ \times [(-i\omega_3 + \hat{D})^{-1} \hat{L}]_{\sigma\lambda} + l_{\tau,v\gamma} [\hat{R}^{-1} (-i\omega_3 + \hat{D})^{-1} \hat{L}]_{\gamma\lambda} \\ + l_{\tau,\beta\lambda} [\hat{R}^{-1} (-i\omega_2 + \hat{D})^{-1} \hat{L}]_{\beta v} + l_{\tau,v\lambda} \} \delta(\omega_1 + \omega_2 + \omega_3), \quad (6.1.14)$$

where

$$\hat{L} = \|l_{\tau,\beta}\|, \quad \hat{R} = \|r_{\gamma\rho}\|. \quad (6.1.15)$$

Let us now denote

$$l_{\tau,\beta} s_{\beta\rho\sigma} + l_{\tau,\beta\gamma} r_{\beta\rho}^{-1} r_{\gamma\sigma}^{-1} = f_{\tau\rho\sigma} \quad (6.1.16)$$

and substitute $l_{\tau,\beta\gamma} = (f_{\tau\rho\sigma} - l_{\tau,\beta} s_{\beta\rho\sigma}) r_{\rho\beta} r_{\sigma\gamma}$ into (6.1.14). We can now combine the terms in braces that contain $f_{\tau\rho\sigma}$ by applying the equation

$$(-i\omega + \hat{D})^{-1} \hat{L} + \hat{R} = (-i\omega + \hat{D})^{-1} [\hat{L} + (-i\omega - \hat{L}\hat{R}^{-1})\hat{R}] \\ = -i\omega (-i\omega + \hat{D})^{-1} \hat{R}, \quad (6.1.17)$$

where (6.1.5) is used. Hence, (6.1.14) assumes the form

$$\begin{aligned} G_{\mu, v\lambda}(\omega_1, \omega_2, \omega_3) &= (2\pi)^{-1/2} (i\omega_1 + \hat{D})_{\mu\tau}^{-1} \{ f_{\tau\rho\sigma} i\omega_2 i\omega_3 ((-i\omega_2 + \hat{D})^{-1} \hat{R})_{\rho\nu} \\ &\quad \times ((-i\omega_3 + \hat{D})^{-1} \hat{R})_{\sigma\lambda} - l_{\tau, \beta} s_{\beta\rho\sigma} [r_{\rho\nu} (-i\omega_3 + \hat{D})_{\sigma\kappa}^{-1} l_{\kappa, \lambda} \\ &\quad + r_{\rho\lambda} (-i\omega_2 + \hat{D})_{\sigma\kappa}^{-1} l_{\kappa, \nu} + r_{\rho\nu} r_{\sigma\lambda}] \} \delta(\omega_1 + \omega_2 + \omega_3). \end{aligned} \quad (6.1.18)$$

Employing again (6.1.17) to transform the three terms in brackets in (6.1.18), we eventually obtain

$$\begin{aligned} G_{1, 23} &= (2\pi)^{-1/2} \{ (i\omega_1 + \hat{D})_{\alpha_1\tau}^{-1} f_{\tau\rho\sigma} i\omega_2 i\omega_3 \\ &\quad \times [(-i\omega_2 + \hat{D})^{-1} \hat{R}]_{\rho\alpha_2} [(-i\omega_3 + \hat{D})^{-1} \hat{R}]_{\sigma\alpha_3} \\ &\quad + i\omega_3 U_{123} + i\omega_2 U_{132} + W_{123} \} \delta(\omega_1 + \omega_2 + \omega_3), \end{aligned} \quad (6.1.19)$$

where

$$U_{123} = (i\omega_1 + \hat{D})_{\alpha_1\tau}^{-1} l_{\tau, \beta} s_{\beta\rho\sigma} r_{\rho\alpha_2} (-i\omega_3 + \hat{D})_{\sigma\alpha_3}^{-1} r_{\lambda\alpha_3}, \quad (6.1.20)$$

$$W_{123} = (i\omega_1 + \hat{D})_{\alpha_1\tau}^{-1} l_{\tau, \beta} s_{\beta\rho\sigma} r_{\rho\alpha_2} r_{\sigma\alpha_3} \equiv (i\omega_1 + \hat{D}_1)^{-1} \hat{L}_1 s_{123} \hat{R}_2 \hat{R}_3. \quad (6.1.21)$$

Note that the factor $[(-i\omega_3 + \hat{D})^{-1} \hat{R}]_{\sigma\alpha_3}$ in (6.1.20) can be placed to the right of $s_{\beta\rho\sigma}$, so that

$$\begin{aligned} U_{123} &= [(i\omega_1 + \hat{D})^{-1} \hat{L}]_{\alpha_1\beta} [\hat{R} (-i\omega_3 + \hat{D}^T)^{-1}]_{\alpha_3\sigma} s_{\beta\rho\sigma} r_{\rho\alpha_3} \\ &\equiv (i\omega_1 + \hat{D}_1)^{-1} \hat{L}_1 \hat{R}_3 (-i\omega_3 + \hat{D}_3^T)^{-1} s_{123} \hat{R}_2. \end{aligned} \quad (6.1.22)$$

We have thus found the linear and quadratic admittances in the spectral representation.

6.1.2 Twofold and Threefold Correlators in the Markov Case

From the fluctuation-dissipation relations derived in Sect. 5.3, we can readily obtain twofold and threefold correlators. If we substitute (6.1.12) into (5.3.11) taken in the spectral representation, i.e. into

$$\langle B_1, B_2 \rangle = -\frac{kT}{i\omega_1} [G_{\alpha_1, \alpha_2}(\omega_1, \omega_2) - G_{\alpha_2, \alpha_1}(\omega_2, \omega_1)], \quad (6.1.23)$$

and take into account that

$$\begin{aligned} (i\omega_1 + \hat{D})^{-1} \hat{L} - \hat{L}^T (-i\omega_1 + \hat{D}^T)^{-1} &= (i\omega_1 + \hat{D})^{-1} [\hat{L} (-i\omega_1 - \hat{R} \hat{L}^T) - (i\omega_1 - \hat{L} \hat{R}) \hat{L}^T] (-i\omega_1 + \hat{D}^T)^{-1} \\ &= -i\omega_1 (i\omega_1 + \hat{D})^{-1} (\hat{L} + \hat{L}^T) (-i\omega_1 + \hat{D}^T)^{-1}, \end{aligned} \quad (6.1.24)$$

where we have used (6.1.6), we will have

$$\langle B_1, B_2 \rangle = -kT (i\omega_1 + \hat{D})^{-1} (\hat{L} + \hat{L}^T) (-i\omega_1 + \hat{D}^T)^{-1} \delta(\omega_1 + \omega_2). \quad (6.1.25)$$

This result corresponds to the spectral density

$$S_{\alpha\beta}(\omega) = -kT[(i\omega + \hat{D})^{-1}(\hat{L} + \hat{L}^T)(-i\omega + \hat{D}^T)^{-1}]_{\alpha\beta}. \quad (6.1.26)$$

This, of course, coincides with (4.4.14), derived earlier by another method.

Let us now substitute (6.1.19) into FDR (5.3.72) at $p_i = i\omega_i$ and find the spectral form of the threefold correlator:

$$\begin{aligned} \beta^2 \langle B_1, B_2, B_3 \rangle &= (2\pi)^{-1/2} P_{(123)}[(i\omega_1 + \hat{D}_1)^{-1} f_{123}(-i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 \\ &\quad \times (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 \\ &\quad + \varepsilon_1 \varepsilon_2 \varepsilon_3 (-i\omega_1 + \hat{D}_1)^{-1} f_{123}(i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 \\ &\quad \times (i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 + (i\omega_2)^{-1} (U_{123} - U_{123}^{t.c.}) \\ &\quad + (i\omega_3)^{-1} (U_{132} - U_{132}^{t.c.}) + (i\omega_2 i\omega_3)^{-1} \\ &\quad \times (W_{123} + W_{123}^{t.c.})] \delta(\omega_1 + \omega_2 + \omega_3). \end{aligned} \quad (6.1.27)$$

Here, as usual, $P_{(123)}$ stands for the sum over cyclic permutations of subscripts 1, 2, 3; the first two terms are written using the same abbreviated matrix notation as in (6.1.21, 22).

Considering that

$$(p_1 + \hat{D})^{-1} \hat{D} = 1 - p_1(p_1 + \hat{D})^{-1} = 1 + (p_2 + p_3)(p_1 + \hat{D})^{-1},$$

we obtain

$$p_2^{-1} p_3^{-1} (p_1 + \hat{D})^{-1} \hat{D} = p_2^{-1} p_3^{-1} + (p_3^{-1} + p_2^{-1})(p_1 + \hat{D})^{-1}. \quad (6.1.28)$$

Using (6.1.28) and (6.1.5) and substituting (6.1.21) into the expression $P_{(123)}(i\omega_2 i\omega_3)^{-1} W_{123}$ gives

$$\begin{aligned} P_{(123)}(i\omega_2 i\omega_3)^{-1} W_{123} &= -P_{(123)}\{[(i\omega_2)^{-1} + (i\omega_3)^{-1}] \\ &\quad \times (i\omega_1 + \hat{D}_1)^{-1}\} \hat{R}_1 \hat{R}_2 \hat{R}_3 s_{123}, \end{aligned} \quad (6.1.29)$$

because

$$P_{(123)}[\omega_1^{-1} \omega_2^{-1}] = \omega_1^{-1} \omega_2^{-1} \omega_3^{-1} (\omega_1 + \omega_2 + \omega_3) = 0 \quad (6.1.30)$$

by virtue of the condition $\omega_1 + \omega_2 + \omega_3 = 0$.

From (6.1.29) we find

$$\begin{aligned} P_{(123)}(i\omega_2 i\omega_3)^{-1} W_{123}^{t.c.} &= P_{(123)} \varepsilon_1 \varepsilon_2 \varepsilon_3 [(i\omega_2)^{-1} + (i\omega_3)^{-1}] \\ &\quad \times (-i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 \hat{R}_2 \hat{R}_3 s_{123}. \end{aligned} \quad (6.1.31)$$

The following reciprocal relations also hold:

$$\varepsilon \hat{D} \hat{R} \varepsilon = \hat{R} \hat{D}^T, \quad (6.1.32a)$$

$$\varepsilon (i\omega + \hat{D})^{-1} \hat{R} \varepsilon = \hat{R} (i\omega + \hat{D}^T)^{-1}, \quad (6.1.32b)$$

$$\varepsilon (i\omega + \hat{D})^{-1} \hat{L} \varepsilon = \hat{L}^T (i\omega + \hat{D}^T)^{-1}. \quad (6.1.32c)$$

The first of these is equivalent to the relationship $\varepsilon L\varepsilon = L^T$, i.e. to (4.1.13), the second follows from the first, and the third is equivalent to the reciprocal relation (5.3.47). If we make use of (6.1.32b) and the relations

$$\begin{aligned} \varepsilon \hat{R} \varepsilon &= \hat{R}, \\ \varepsilon_1 \varepsilon_2 \hat{R}_1 \varepsilon_3 \hat{R}_3 s_{123} &= \hat{R}_2 \hat{R}_3 \varepsilon_1 \varepsilon_2 \varepsilon_3 s_{123} = \hat{R}_2 \hat{R}_3 s_{123}, \end{aligned} \quad (6.1.33)$$

which follow from the condition that the free energy and one-time equilibrium probability density are time-reversal invariants, (6.1.31) will reduce to the form

$$\begin{aligned} P_{(123)}(i\omega_2 i\omega_3)^{-1} W_{123}^{t,c} \\ = P_{(123)}[(i\omega_2)^{-1} + (i\omega_3)^{-1}] \hat{R}_1(-i\omega_1 + \hat{D}_1^T)^{-1} \hat{R}_2 \hat{R}_3 s_{123}. \end{aligned} \quad (6.1.34)$$

If then we add (6.1.29) and (6.1.34) together and rearrange the terms, we have

$$\begin{aligned} P_{(123)}(i\omega_2 i\omega_3)^{-1} (W_{123} + W_{123}^{t,c}) \\ = -P_{(123)}(i\omega_2)^{-1} \{ [(i\omega_1 + \hat{D}_1)^{-1} \hat{R}_3 - \hat{R}_3(-i\omega_3 + \hat{D}_3^T)^{-1}] \hat{R}_1 \\ + [(i\omega_3 + \hat{D}_3)^{-1} \hat{R}_1 - \hat{R}_1(-i\omega_1 + \hat{D}_1^T)^{-1}] \hat{R}_3 \} s_{123} \hat{R}_2. \end{aligned} \quad (6.1.35)$$

Let us now look at those terms in (6.1.27) that contain U_{123} . Rearranging these terms gives

$$\begin{aligned} P_{(123)}[(i\omega_2)^{-1}(U_{123} - U_{123}^{t,c}) + (i\omega_3)^{-1}(U_{132} - U_{132}^{t,c})] \\ = P_{(123)}(i\omega_2)^{-1} [(U_{123} - U_{321}^{t,c}) + (U_{321} - U_{123}^{t,c})]. \end{aligned} \quad (6.1.36)$$

Substituting (6.1.22) and its time conjugate

$$U_{123}^{t,c} = \hat{L}_1^T(-i\omega_1 + \hat{D}_1^T)^{-1}(i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 s_{123} \hat{R}_2 \quad (6.1.37)$$

derived using (6.1.32, 33) gives

$$\begin{aligned} P_{(123)} \{ P_{23}[(i\omega_2)^{-1}(U_{123} - U_{123}^{t,c})] \} \\ = P_{(123)}(i\omega_2)^{-1} P_{13} \{ (i\omega_1 + \hat{D}_1)^{-1} \hat{L}_1 \hat{R}_3(-i\omega_3 + \hat{D}_3^T)^{-1} \\ - (i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 \hat{L}_3^T(-i\omega_3 + \hat{D}_3^T)^{-1} \} s_{123} \hat{R}_2 \\ = -P_{(123)}(i\omega_2)^{-1} P_{13} \{ \hat{R}_3[(i\omega_1 + \hat{D}_1)^{-1} \hat{D}_1(-i\omega_3 + \hat{D}_3^T)^{-1} \\ - (i\omega_1 + \hat{D}_1)^{-1} \hat{D}_3^T(-i\omega_3 + \hat{D}_3^T)^{-1}] \hat{R}_1 \} s_{123} \hat{R}_2. \end{aligned} \quad (6.1.38)$$

The expression in brackets can be written as

$$\begin{aligned} &(i\omega_1 + \hat{D}_1)^{-1} (\hat{D}_1 - \hat{D}_3^T)(-i\omega_3 + \hat{D}_3^T)^{-1} \\ &= (i\omega_1 + \hat{D}_1)^{-1} (i\omega_1 + \hat{D}_1 + i\omega_2 + i\omega_3 - \hat{D}_3^T)(-i\omega_3 + \hat{D}_3^T)^{-1} \\ &= (-i\omega_3 + \hat{D}_3^T)^{-1} - (i\omega_1 + \hat{D}_1)^{-1} + i\omega_2(i\omega_1 + \hat{D}_1)^{-1}(-i\omega_3 + \hat{D}_3^T)^{-1}. \end{aligned} \quad (6.1.39)$$

Therefore, (6.1.38) takes the form

$$\begin{aligned} & P_{(123)} P_{23} [(i\omega_2)^{-1} (U_{123} - U_{123}^{\text{rc}})] \\ &= -P_{(123)} \{ P_{13} [(i\omega_1 + \hat{D}_1)^{-1} \hat{R}_3 (-i\omega_3 + \hat{D}_3^T)^{-1} \hat{R}_1 s_{123} \hat{R}_2] \} \\ &\quad + P_{(123)} (i\omega_2)^{-1} P_{13} \{ [(i\omega_1 + \hat{D}_1)^{-1} \hat{R}_3 \\ &\quad - \hat{R}_3 (-i\omega_3 + \hat{D}_3^T)^{-1}] \hat{R}_1 \} s_{123} \hat{R}_2 . \end{aligned} \quad (6.1.40)$$

When (6.1.35) and (6.1.40) are added together, the terms with the factor $(i\omega_i)^{-1}$ cancel out. The sum $P_{(123)}(P_{13\dots})$ is nothing but the sum $P_{123\dots}$ over all the permutations of the subscripts 1, 2, 3. As a result, from (6.1.27) we get, in the spectral representation,

$$\begin{aligned} & \beta^2 \langle B_1, B_2, B_3 \rangle \\ &= (2\pi)^{-1/2} \{ P_{(123)} [(i\omega_1 + \hat{D}_1)^{-1} f_{123} (-i\omega_2 + \hat{D}_2)^{-1} \\ &\quad \times \hat{R}_2 (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 + \varepsilon_1 \varepsilon_2 \varepsilon_3 (-i\omega_1 + \hat{D}_1)^{-1} \\ &\quad \times f_{123} (i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 (i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3] \\ &\quad - P_{123} [(i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 s_{123} \hat{R}_2 (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3] \} \\ &\quad \times \delta(\omega_1 + \omega_2 + \omega_3) \end{aligned} \quad (6.1.41)$$

or, in the time representation,

$$\begin{aligned} & \beta^2 \langle B_1, B_2, B_3 \rangle \\ &= P_{(123)} \left\{ \int \hat{V}_{\alpha_1 \beta}(t_{10}) f_{\beta \gamma \delta} [\hat{V}(t_{02}) \hat{R}]_{\gamma \alpha_2} [\hat{V}(t_{03}) \hat{R}]_{\delta \alpha_3} dt_0 \right. \\ &\quad \left. + \int [\hat{V}(t_{20}) \hat{R}]_{\alpha_2 \gamma} [\hat{V}(t_{30}) \hat{R}]_{\alpha_3 \delta} \varepsilon_\gamma \varepsilon_\delta f_{\beta \gamma \delta} \varepsilon_\beta r_{\beta \sigma} (\hat{V}(t_{01}) \hat{R})_{\sigma \alpha_1} dt_0 \right\} \\ &\quad - P_{123} \{ [V(t_{12}) \hat{R}]_{\alpha_1 \beta} s_{\beta \gamma \delta} r_{\gamma \alpha_2} [\hat{V}(t_{23}) \hat{R}]_{\delta \alpha_3} \} . \end{aligned} \quad (6.1.42)$$

The condition $V_{\alpha \beta}(t) = 0$ at $t < 0$ dictates that the first integral is taken between $t_m = \max(t_2, t_3)$ and t_1 , and the second one between t_1 and $\min(t_2, t_3)$. Let us proceed to take the integrals. Denote

$$\begin{aligned} F_{123} &= \int_{t_m}^{t_1} V_{\alpha_1 \beta}(t_{10}) f_{\beta \gamma \delta} V_{\gamma \alpha_2}(t_{02}) V_{\delta \alpha_3}(t_{03}) dt_0 \\ &= \int_{t_m}^{t_1} \hat{V}_1(t_{10}) f_{123} \hat{V}_2(t_{02}) \hat{V}_3(t_{03}) dt_0 . \end{aligned} \quad (6.1.43)$$

Using (6.1.7), we obtain

$$\begin{aligned} F_{123} &= \int_{t_m}^{t_1} \exp(-\hat{D}_1 t_{10}) f_{123} \exp(-\hat{D}_2 t_{02} - \hat{D}_3 t_{03}) dt_0 \\ &= \int_{t_m}^{t_1} \exp(\hat{D}_1 t_{01} - \hat{D}_2^T t_{02} - \hat{D}_3^T t_{03}) dt_0 f_{123} . \end{aligned} \quad (6.1.44)$$

Taking the integrals gives

$$F_{123} = [\exp(-\hat{D}_2^T t_{12} - \hat{D}_3^T t_{13}) - \exp(-\hat{D}_1 t_{1m} - \hat{D}_2^T t_{m2} - \hat{D}_3^T t_{m3})] \\ \times (\hat{D}_1 - \hat{D}_2^T - \hat{D}_3^T)^{-1} f_{123}, \quad (6.1.45)$$

i.e.

$$F_{123} = m_{123} \hat{V}_2(t_{12}) \hat{V}_3(t_{13}) - \hat{V}_1(t_{1m}) m_{123} \hat{V}_2(t_{m2}) \hat{V}_3(t_{m3}), \quad (6.1.46)$$

where $m_{123} = (\hat{D}_1 - \hat{D}_2^T - \hat{D}_3^T)^{-1} f_{123}$. This matrix is nothing but a solution of the set of linear equations

$$(\hat{D}_1 - \hat{D}_2^T - \hat{D}_3^T) m_{123} = f_{123},$$

i.e.

$$d_{\alpha\sigma} m_{\alpha\beta\gamma} - m_{\alpha\sigma\gamma} d_{\sigma\beta} - m_{\alpha\beta\sigma} d_{\sigma\gamma} = f_{\alpha\beta\gamma}. \quad (6.1.47)$$

The function (6.1.46) is only nonzero if t_1 is larger than both t_2 and t_3 . If we now introduce the function $H_{123} = F_{123}\eta(t_{23})$, which by virtue of (6.1.46) is

$$H_{123} = m_{123} \hat{V}_1(t_{12}) \hat{V}_3(t_{13}) \eta(t_{23}) - \hat{V}_1(t_{12}) m_{123} \hat{V}_3(t_{23}), \quad (6.1.48)$$

then it will only be nonzero in the region $t_1 \geq t_2 \geq t_3$. Using (6.1.48) we can write (6.1.42) as follows:

$$\beta^2 \langle B_1, B_2, B_3 \rangle = P_{123} \{ [H_{\alpha_1\gamma\delta}(t_1, t_2, t_3) + \epsilon_{\alpha_1} \epsilon_{\alpha_2} \epsilon_{\alpha_3} H_{\alpha_1\gamma\delta}(-t_1, -t_2, -t_3)] \\ \times r_{\gamma\alpha_2} r_{\delta\alpha_3} \} - P_{123} \{ [\hat{V}(t_{12}) \hat{R}]_{\alpha_1\beta} s_{\beta\gamma\delta} r_{\gamma\alpha_2} [\hat{V}(t_{23}) \hat{R}]_{\delta\alpha_3} \}, \quad (6.1.49)$$

where P_{123} is the sum over all the permutations of subscripts 1, 2, 3 which contains six terms. If now in (6.1.49) we let $t_1 \geq t_2 \geq t_3$ and take into account that the functions

$$[\hat{V}(t_{12}) \hat{R}]_{\alpha_1\beta} s_{\beta\gamma\delta} r_{\gamma\alpha_2} [\hat{V}(t_{23}) \hat{R}]_{\delta\alpha_3}$$

are distinct from zero only for $t_1 \geq t_2 \geq t_3$, as in (6.1.48), we arrive at

$$\beta^2 \langle B_{\alpha_1}(t_1), B_{\alpha_2}(t_2), B_{\alpha_3}(t_3) \rangle \\ = [H_{\alpha_1\gamma\delta}(t_1, t_2, t_3) r_{\delta\alpha_3} + \epsilon_{\alpha_1} \epsilon_{\alpha_2} \epsilon_{\alpha_3} H_{\alpha_3\gamma\delta}(-t_3, -t_2, -t_1) r_{\delta\alpha_1} \\ - V_{\alpha_1\rho}(t_{12}) r_{\rho\beta} s_{\beta\gamma\delta} V_{\delta\sigma}(t_{23}) r_{\sigma\alpha_3}] r_{\gamma\alpha_2} \quad (6.1.50)$$

for $t_1 \geq t_2 \geq t_3$.

The set of linear equations (6.1.47), which serves to determine the matrix $m_{\alpha\beta\gamma}$ that enters into (6.1.46), can be solved, in particular, by reducing the matrix $d_{\alpha\beta}$ to the diagonal form. Note that (6.1.50) can be derived through the master equation that describes a given Markov process $B(t)$.

6.1.3 Another Approach to the Computation of Twofold and Threefold Correlators: The Impedance Method

Instead of the method just described of finding the correlators, in which admittances are calculated initially, another technique can be used that yields the result faster; this we will now discuss.

To begin with, we will change the variables: we introduce quantities A' (functions of A), such that the derivative of free energy $F'(A') = F[A(A')]$ with respect to A'_α is equal to A_α :

$$\partial F'(A')/\partial A'_\alpha = A_\alpha . \quad (6.1.51)$$

Differentiating (6.1.51) as a composite function gives

$$\frac{\partial F}{\partial A_\beta} \frac{\partial A_\beta}{\partial A'_\alpha} = A_\alpha . \quad (6.1.52)$$

In the one-component case, this equation is readily solved for $\partial A'_\alpha/\partial A_\beta \equiv \partial A'_1/\partial A_1$ to find $dA'_1/dA_1 = A_1^{-1} \partial F/\partial A_1$. Substituting the one-component form of (6.1.2), we will have

$$dA'_1/dA_1 = r_{11}^{-1} + \frac{1}{2}s_{111}A_1 . \quad (6.1.53)$$

Integrating gives

$$A'_1(A_1) = r_{11}^{-1}A_1 + \frac{1}{4}s_{111}A_1^2 . \quad (6.1.54)$$

In the many-component case, (6.1.54) has the form

$$A'_\alpha(A) = r_{\alpha\beta}^{-1}A_\beta + \frac{1}{4}s_{\alpha\beta\gamma}A_\beta A_\gamma . \quad (6.1.55)$$

Solving (6.1.55) for A , we obtain

$$A_\beta(A') = r_{\beta\alpha}(A'_\alpha - \frac{1}{4}s_{\alpha\gamma\delta}r_{\gamma\rho}r_{\delta\sigma}A'_\rho A'_\sigma) + O((A')^3) . \quad (6.1.56)$$

Hence,

$$\begin{aligned} \partial A_\beta / \partial A'_\alpha &= r_{\beta\alpha} - \frac{1}{2}r_{\beta\sigma}s_{\sigma\gamma\delta}r_{\gamma\rho}r_{\delta\alpha}A'_\rho \\ &= r_{\beta\alpha} - \frac{1}{2}r_{\beta\sigma}s_{\sigma\gamma\delta}A_\gamma r_{\delta\alpha} + O(A^2) . \end{aligned} \quad (6.1.57)$$

Substituting (6.1.57) and (6.1.2) into (6.1.52), we can easily see that (6.1.52) holds, thus confirming the many-component formula (6.1.55) in terms of the chosen approximation.

Let us now find the derivative of A' with respect to time. From (6.1.55) we obtain

$$\dot{A}'_\alpha = (r_{\alpha\beta}^{-1} + \frac{1}{2}s_{\alpha\beta\gamma}A_\gamma)\dot{A}_\beta . \quad (6.1.58)$$

We will now substitute (6.1.1), where x must be expressed in terms of A :

$$x_\alpha = \partial F(A_\alpha)/\partial A_\alpha = r_{\alpha\beta}^{-1}A_\beta + \frac{1}{2}s_{\alpha\beta\gamma}A_\beta A_\gamma .$$

With the notation used in (6.1.5) and (6.1.16), we obtain

$$\begin{aligned} \dot{A}'_\alpha &= (r_{\alpha\beta}^{-1} + \frac{1}{2}s_{\alpha\beta\gamma}A_\gamma)(-d_{\beta\rho}A_\rho + \frac{1}{2}f_{\beta\rho\sigma}A_\rho A_\sigma) \\ &= -r_{\alpha\beta}^{-1}d_{\beta\rho}A_\rho + \frac{1}{2}(r_{\alpha\beta}^{-1}f_{\beta\rho\sigma} - s_{\alpha\beta\rho}d_{\beta\sigma})A_\rho A_\sigma . \end{aligned} \quad (6.1.59)$$

This equation can be viewed as another form of (6.1.1). In fact, instead of A we have here the equivalent variables A' . According to (6.1.51), for these variables the parameters A play the role of the forces x' conjugate to A' ; and $-r_{\alpha\beta}^{-1}d_{\beta\rho}$ can be interpreted as $l'_{\alpha,\rho}$, and $r_{\alpha\beta}^{-1}f_{\beta\rho\sigma} - (s_{\alpha\beta\rho}d_{\beta\sigma} + s_{\alpha\beta\sigma}d_{\beta\rho})/2$ as $l'_{\alpha,\rho\sigma}$.

We will now introduce external forces into (6.1.59) (where they have so far been absent) but not according to the recipe (6.1.3). It is worth noting here that \dot{A}' has the character of a force conjugate of the parameter

$$\tilde{A}_\alpha = \int A_\alpha(t) dt . \quad (6.1.60)$$

The integral here is an indefinite one.

According to (6.1.51), A' and A are thermodynamically conjugate parameters and their product $A'A$ has the meaning of energy. Therefore, $\dot{A}'\tilde{A}$ also has the meaning of energy, and so these parameters are thermodynamically conjugate. That \dot{A}' represents a force conjugate of \tilde{A} is seen especially well with reference to examples (see, for instance, Sects. 6.2.1 and 6.2.4). Let us now introduce into (6.1.59) the external forces \tilde{h}_α conjugate to A_α

$$\dot{A}'_\alpha - \tilde{h}_\alpha = -r_{\alpha\beta}^{-1} d_{\beta\rho} A_\rho + \frac{1}{2}(r_{\alpha\beta}^{-1} f_{\beta\rho\sigma} - s_{\alpha\beta\rho} d_{\beta\sigma}) A_\rho A_\sigma . \quad (6.1.61)$$

The sign of \tilde{h}_α is chosen here so that in a stable state (if only at small forces) the vector A_α will be directed in about the same direction as vector \tilde{h}_α . In reality, putting $\dot{A}'_\alpha = 0$, we obtain from (6.1.61) in a linear approximation $r_{\alpha\beta}^{-1} d_{\beta\rho} A_\rho = \tilde{h}_\alpha$. From this and (6.1.5) we obtain the scalar product of A_α and \tilde{h}_α :

$$\begin{aligned} A_\alpha \tilde{h}_\alpha &= r_{\alpha\beta}^{-1} d_{\beta\rho} A_\alpha A_\rho \\ &= -l_{\alpha,\beta} r_{\alpha\sigma}^{-1} r_{\beta\rho}^{-1} A_\sigma A_\rho \\ &= -\frac{1}{2}(l_{\alpha,\beta} + l_{\beta,\alpha}) r_{\alpha\sigma}^{-1} r_{\beta\rho}^{-1} A_\sigma A_\rho . \end{aligned} \quad (6.1.62)$$

Using (4.1.12), we derive from (6.1.62)

$$A_\alpha \tilde{h}_\alpha = (2kT)^{-1} l_{\alpha\beta} r_{\alpha\sigma}^{-1} r_{\beta\rho}^{-1} A_\sigma A_\rho . \quad (6.1.63)$$

The right-hand side here is positive for the same reason that the right-hand side of (4.6.4) is negative. Hence, $A_\alpha \tilde{h}_\alpha > 0$, whereby the direction of A_α stated above is confirmed. A similar rule concerning the direction of displacement under the action of forces holds if the latter are introduced according to (6.1.3).

By virtue of (6.1.58), equation (6.1.61) can be written as

$$(r_{\alpha\beta}^{-1} + \frac{1}{2}s_{\alpha\beta\rho} A_\rho) \dot{A}_\beta + r_{\alpha\beta}^{-1} d_{\beta\rho} A_\rho - \frac{1}{2}(r_{\alpha\beta}^{-1} f_{\beta\rho\sigma} - s_{\alpha\beta\rho} d_{\beta\sigma}) A_\rho A_\sigma = \tilde{h}_\alpha . \quad (6.1.64)$$

In relation to the variable (6.1.60), the parameter A_α is the flux: $\tilde{J}_\alpha = \dot{A}_\alpha = A_\alpha$. It follows that if we write p instead of the time derivative, we will have

$$r_{\alpha\beta}^{-1}(p\delta_{\beta\rho} + d_{\beta\rho}) \tilde{J}_\rho - \frac{1}{2}r_{\alpha\beta}^{-1} f_{\beta\rho\sigma} \tilde{J}_\rho \tilde{J}_\sigma + \frac{1}{2}s_{\alpha\beta\rho} \tilde{J}_\rho(p\delta_{\beta\sigma} + d_{\beta\sigma}) \tilde{J}_\sigma = \tilde{h}_\alpha . \quad (6.1.65)$$

This equation is a special case of (5.6.8), and comparison of these equations yields the linear and quadratic impedances

$$\tilde{Z}_{\alpha_1\alpha_2}(t_1, t_2) = r_{\alpha_1\beta}^{-1}(-p_2\delta_{\beta\alpha_2} + d_{\beta\alpha_2})\delta(t_1 - t_2) \quad (6.1.66a)$$

$$\begin{aligned} \tilde{Z}_{\alpha_1,\alpha_2,\alpha_3}(t_1, t_2, t_3) &= [-r_{\alpha_1\beta}^{-1} f_{\beta\alpha_2\alpha_3} + \frac{1}{2}s_{\alpha_1\beta\alpha_3}(-p_2\delta_{\beta\alpha_2} + d_{\beta\alpha_2}) \\ &\quad + \frac{1}{2}s_{\alpha_1\beta\alpha_3}(-p_3\delta_{\beta\alpha_3} + d_{\beta\alpha_3})]\delta(t_1, t_2, t_3) . \end{aligned} \quad (6.1.66b)$$

Knowing the impedances, we can use the relations

$$\begin{aligned} Y_{1,2} &= Z_{1,2}^{-1} \\ Y_{1,23} &= Y_1 Z_{1,23} Y_2 Y_3 , \end{aligned} \quad (6.1.67)$$

which are equivalent to (5.6.6a, b), to find the respective admittances.

From formula (6.1.66a), which can be written as $\hat{Z}(\omega_1, \omega_2) = \hat{R}^{-1}(i\omega_2 \hat{I} + \hat{D})\delta(\omega_1 + \omega_2)$, we obtain, using (6.1.67),

$$\tilde{Y}_{1,2} = [(i\omega_1 \hat{I} + \hat{D})^{-1} \hat{R}]_{\alpha_1 \alpha_2} \delta(\omega_1 + \omega_2) \quad (6.1.68)$$

and from (6.1.66b) we get

$$\begin{aligned} \tilde{Y}_{1,23} &= (2\pi)^{-1/2} (i\omega_1 + \hat{D})_{\alpha_1 \beta}^{-1} \{ f_{\beta \gamma \delta} [(-i\omega_2 + \hat{D})^{-1} \hat{R}]_{\gamma \alpha_2} \\ &\quad \times [(-i\omega_3 + \hat{D})^{-1} \hat{R}]_{\delta \alpha_3} - \frac{1}{2} r_{\alpha_1 \beta} s_{\beta \gamma \delta} [r_{\gamma \alpha_2} [(-i\omega_3 + \hat{D})^{-1} \hat{R}]_{\delta \alpha_3} \\ &\quad + [(-i\omega_2 + \hat{D})^{-1} R]_{\gamma \alpha_2} r_{\delta \alpha_3}] \} \delta(\omega_1 + \omega_2 + \omega_3) . \end{aligned} \quad (6.1.69)$$

To find the correlator $\langle \tilde{J}_1, \tilde{J}_2, \tilde{J}_3 \rangle_0 \equiv \langle B_1, B_2, B_3 \rangle_0$ we will now have to use the FDR (5.3.75), i.e.

$$\beta^2 Y_{123} = P_{(123)}(Y_{1,23} - Y_{1,23}^{t.c.}) . \quad (6.1.70)$$

Using (6.1.69) we then obtain

$$\begin{aligned} &\beta^2 \langle B_1, B_2, B_3 \rangle \\ &= (2\pi)^{-1/2} P_{(123)} \{ (i\omega_1 + \hat{D}_1)^{-1} f_{123} (-i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 \\ &\quad - \tilde{\varepsilon}_1 \tilde{\varepsilon}_2 \tilde{\varepsilon}_3 (-i\omega_1 + \hat{D}_1)^{-1} f_{123} (i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 (i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 \\ &\quad - \frac{1}{2} P_{23} [N_{\alpha_1 \alpha_2 \alpha_3}(\omega_1, \omega_2, \omega_3) \\ &\quad - \tilde{\varepsilon}_1 \tilde{\varepsilon}_2 \tilde{\varepsilon}_3 N_{\alpha_1 \alpha_2 \alpha_3}(-\omega_1, -\omega_2, -\omega_3)] \} \delta(\omega_1 + \omega_2 + \omega_3) , \end{aligned} \quad (6.1.71)$$

where

$$N_{\alpha_1 \alpha_2 \alpha_3}(\omega_1, \omega_2, \omega_3) = (i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 s_{123} \hat{R}_2 (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 . \quad (6.1.72)$$

The first term in braces on the right-hand side of (6.1.71) coincides with the corresponding term in (6.1.41). The second term also coincides, since $\tilde{\varepsilon}_\alpha = -\varepsilon_\alpha$ (this means that A_α and the parameter (6.1.60) have different time parities).

It is easily seen that the sums of the remaining terms in (6.1.71) and (6.1.41) also coincide. In fact, from (6.1.32b) and the equality $\varepsilon_1 \varepsilon_2 \varepsilon_3 s_{123} = s_{123}$, we can readily obtain

$$\begin{aligned} &- \tilde{\varepsilon}_{\alpha_1} \tilde{\varepsilon}_{\alpha_2} \tilde{\varepsilon}_{\alpha_3} N_{\alpha_3 \alpha_2 \alpha_1}(-\omega_3, -\omega_2, -\omega_1) \\ &= \varepsilon_2 \varepsilon_3 (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 s_{123} \hat{R}_2 (i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 \varepsilon_1 \\ &= \hat{R}_3 (-i\omega_3 + \hat{D}_3^\top)^{-1} \varepsilon_3 s_{123} \varepsilon_2 \varepsilon_1 \hat{R}_2 \hat{R}_1 (i\omega_1 + \hat{D}_1^\top)^{-1} \\ &= (i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 s_{123} \hat{R}_2 (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 , \end{aligned} \quad (6.1.73)$$

i.e.

$$- \tilde{\varepsilon}_{\alpha_1} \tilde{\varepsilon}_{\alpha_2} \tilde{\varepsilon}_{\alpha_3} N_{\alpha_3 \alpha_2 \alpha_1}(-\omega_3, -\omega_2, -\omega_1) = N_{\alpha_1 \alpha_2 \alpha_3}(\omega_1, \omega_2, \omega_3) . \quad (6.1.74)$$

However, the sum $P_{(123)}(P_{23}N_{123})$ is nothing but the sum $P_{123}N_{123}$ over all the permutations.

Thus, using impedances \tilde{Z}_{12} and \tilde{Z}_{123} we have obtained the same three-time correlator as obtained using the admittances derived in Sect. 6.1.1. In what follows we will apply the impedance method, since it requires less computation.

By this method we can easily find the derivative

$$\begin{aligned}\tilde{Y}_{12,3} &= \delta\langle\tilde{J}_1, \tilde{J}_2\rangle/\delta\tilde{h}_3, \\ &= \delta\langle B_1, B_2\rangle/\delta\tilde{h}_3, \quad \text{for } \tilde{h} \equiv 0,\end{aligned}\tag{6.1.75}$$

of the twofold correlator with respect to forces. For this purpose, we will have to use the FDR (5.3.99). Considering (6.1.69) we will immediately have

$$\begin{aligned}\beta\tilde{Y}_{12,3} &= (2\pi)^{-1/2} \{ P_{12} [(i\omega_1 + \hat{D}_1)^{-1} f_{123} (-i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 \\ &\quad \times (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3] \\ &\quad + \varepsilon_1 \varepsilon_2 \varepsilon_3 (-i\omega_3 + \hat{D}_3)^{-1} f_{321} (i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 \\ &\quad \times (i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 \\ &\quad - \tfrac{1}{2} P_{12} (2N_{123} + N_{132}) \} \delta(\omega_1 + \omega_2 + \omega_3).\end{aligned}\tag{6.1.76}$$

Here we have made use of (6.1.74). This concludes the calculation of the three-subscript functions.

6.1.4 Finding the Fourfold Correlator: Its Dissipationally Determinable Part

On the assumption that quadratic effects are absent, the phenomenological equation in the linear–cubic approximation takes the form

$$\dot{A}_\alpha = -d_{\alpha\beta} A_\beta + \tfrac{1}{6} f_{\alpha\beta\gamma\delta} A_\beta A_\gamma A_\delta.\tag{6.1.77}$$

In the same approximation the free energy is representable in the form

$$F(A) = \tfrac{1}{2} r_{\alpha\beta}^{-1} A_\alpha A_\beta + \tfrac{1}{24} s_{\alpha\beta\gamma\delta} A_\alpha A_\beta A_\gamma A_\delta.\tag{6.1.78}$$

If we introduce the parameters

$$A'_\alpha(A) = r_{\alpha\beta}^{-1} A_\beta + \tfrac{1}{18} s_{\alpha\beta\gamma\delta} A_\beta A_\gamma A_\delta,\tag{6.1.79}$$

then it can be readily shown that in the approximation chosen they will fulfil (6.1.51). Using (6.1.78, 79), we obtain

$$\begin{aligned}\dot{A}'_\alpha &= (r_{\alpha\beta}^{-1} + \tfrac{1}{6} s_{\alpha\beta\gamma\delta} A_\gamma A_\delta)(-d_{\beta\rho} A_\rho + \tfrac{1}{6} f_{\beta\rho\sigma\tau} A_\rho A_\sigma A_\tau) \\ &= -r_{\alpha\beta}^{-1} d_{\beta\gamma} A_\gamma + \tfrac{1}{6}(r_{\alpha\beta}^{-1} f_{\beta\gamma\delta\rho} - s_{\alpha\beta\gamma\delta} d_{\beta\rho}) A_\gamma A_\delta A_\rho + \dots.\end{aligned}\tag{6.1.80}$$

Here, as in the previous subsection, \dot{A}' has the meaning of a force conjugate of the parameter (6.1.60). Introducing an external force conjugate of this parameter we get

$$\dot{A}'_\alpha - \tilde{h}_\alpha = -r_{\alpha\beta}^{-1} d_{\beta\gamma} A_\gamma + \tfrac{1}{6}(r_{\alpha\beta}^{-1} f_{\beta\gamma\delta\rho} - s_{\alpha\beta\gamma\delta} d_{\beta\rho}) A_\gamma A_\delta A_\rho.\tag{6.1.81}$$

If we insert (6.1.79) and substitute \tilde{J}_α for A_α and p for d/dt , we obtain

$$\tilde{h}_\alpha = r_{\alpha\beta}^{-1}(p\delta_{\beta\gamma} + d_{\beta\gamma})\tilde{J}_\gamma - \frac{1}{6}r_{\alpha\sigma}^{-1}f_{\sigma\beta\gamma\delta}\tilde{J}_\beta\tilde{J}_\gamma\tilde{J}_\delta + \frac{1}{6}s_{\alpha\beta\gamma\delta}\tilde{J}_\gamma\tilde{J}_\delta(p\delta_{\beta\rho} + d_{\beta\rho})\tilde{J}_\rho. \quad (6.1.82)$$

Comparing this with (5.6.8) written in terms of variables $\tilde{h}, \tilde{J}, \tilde{Z}, \dots$ we obtain, in addition to the linear impedance given in (6.1.66a), the cubic impedance in the temporal form

$$\tilde{Z}_{1,234} = [-r_{\alpha_1\beta}^{-1}f_{\beta\alpha_2\alpha_3\alpha_4} + \frac{1}{3}P_{(234)}s_{\alpha_1\beta\alpha_3\alpha_4}(-p_2\hat{I} + \hat{D})_{\beta\alpha_2}]\delta(t_1, t_2, t_3, t_4) \quad (6.1.83)$$

or in the spectral form

$$\begin{aligned} Z_{\alpha_1,\alpha_2\alpha_3\alpha_4}(\omega_1, \dots, \omega_4) &= (2\pi)^{-1}[-r_{\alpha_1\beta}^{-1}f_{\beta\alpha_2\alpha_3\alpha_4} \\ &\quad + \frac{1}{3}P_{(234)}s_{\alpha_1\beta\alpha_3\alpha_4}(i\omega_2\hat{I} + \hat{D})_{\beta\alpha_2}] \\ &\quad \times \delta(\omega_1 + \omega_2 + \omega_3 + \omega_4). \end{aligned} \quad (6.1.84)$$

Here we have symmetrized (in subscripts 2, 3 and 4) the nonsymmetric term. Now, using the relation

$$Y_{1,234} = -Y_1 Z_{1,234} Y_2 Y_3 Y_4, \quad (6.1.85)$$

derived from (5.6.6c) at $Z_{1,23} = 0$, we find from (6.1.68) and (6.1.84) the appropriate admittance

$$\begin{aligned} \tilde{Y}_{1,234} &= (2\pi)^{-1}(i\omega_1 + \hat{D}_1)^{-1}\{f_{1234}(-i\omega_2 + \hat{D}_2)^{-1}\hat{R}_2(-i\omega_3 \\ &\quad + \hat{D}_3)^{-1}\hat{R}_3(-i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4 - \frac{1}{3}P_{(234)}[\hat{R}_1 s_{1234}\hat{R}_2(-i\omega_3 \\ &\quad + \hat{D}_3)^{-1}\hat{R}_3(-i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4]\}\delta(\omega_1 + \dots + \omega_4). \end{aligned} \quad (6.1.86)$$

If we now use (5.4.109c), we can find the dissipationally determinable part of the fourfold correlator $\langle \tilde{J}_1, \dots, \tilde{J}_4 \rangle_0 = \langle B_1, \dots, B_4 \rangle_0$. We thus arrive at

$$\begin{aligned} \beta^3 \langle B_1, B_2, B_3, B_4 \rangle^{(1)} &= (2\pi)^{-1}P_{(1234)}[(i\omega_1 + \hat{D}_1)^{-1}f_{1234} \\ &\quad \times (-i\omega_2 + \hat{D}_2)^{-1}\hat{R}_2(-i\omega_3 \\ &\quad + \hat{D}_3)^{-1}\hat{R}_3(-i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4 \\ &\quad + \varepsilon_1\varepsilon_2\varepsilon_3\varepsilon_4(-i\omega_1 + \hat{D}_1)^{-1}f_{1234}(i\omega_2 \\ &\quad + \hat{D}_2)^{-1}\hat{R}_2(i\omega_3 + \hat{D}_3)^{-1}\hat{R}_3(i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4 \\ &\quad - \frac{1}{3}P_{(234)}(N_{1234} + \bar{N}_{4321})]\delta(\omega_1 + \omega_2 + \omega_3 + \omega_4), \end{aligned} \quad (6.1.87)$$

where

$$\begin{aligned} N_{1234} &= (i\omega_1 + \hat{D}_1)^{-1}\hat{R}_1\hat{R}_2s_{1234}(-i\omega_3 + \hat{D}_3)^{-1}\hat{R}_3(-i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4, \\ \bar{N}_{4321} &= (i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4(i\omega_3 + \hat{D}_3)^{-1}\hat{R}_3s_{1234}\hat{R}_2 \\ &\quad \times (-i\omega_1 + \hat{D}_1)^{-1}\hat{R}_1 = N_{1234}^{t.c.}. \end{aligned} \quad (6.1.88)$$

6.1.5 Dissipationally Undeterminable Functions $Z_{12,34}^{(2)}, Y_{12,34}^{(2)}$

The fourfold correlator is determined not only by the impedance (6.1.83) but also by the dissipationally undeterminable function $Z_{12,34}^{(2)}$, which according to (5.7.56a, b) in the nonquantum case exhibits the following symmetrical behaviour:

$$\tilde{Z}_{12,34}^{(2)} = \tilde{Z}_{21,34}^{(2)} = \tilde{Z}_{12,43}^{(2)} = (\tilde{Z}_{34,12}^{(2)})^{\text{t.c.}}, \quad (6.1.89)$$

The function $Z_{12,34}^{(2)}$, which enters into the relationship

$$Y_{12,34}^{(2)} = Y_1 Y_2 Z_{12,34}^{(2)} Y_3 Y_4 \quad (6.1.90)$$

that is equivalent to (5.7.42), defines the dissipationally undeterminable part of

$$Y_{12,34} = \delta^2 \langle B_1, B_2 \rangle / \delta h_3 \delta h_4 \quad \text{for } h \equiv 0. \quad (6.1.91)$$

If $Y_{12,34}^{(2)}$ is known, then from (5.4.108c) we can find the dissipationally undeterminable part of the correlator

$$\beta^2 \langle \tilde{J}_1, \tilde{J}_2, \tilde{J}_3, \tilde{J}_4 \rangle^{(2)} = P_{(234)} (\tilde{Y}_{12,34}^{(2)} + \tilde{Y}_{23,41}^{(2)}). \quad (6.1.92)$$

We will now proceed to find $Z_{12,34}^{(2)}$ in this case. It has been shown in Sect. 6.1.3 that A_α plays the role of the force x'_α conjugate to A'_α . Therefore, (6.1.80), i.e. the equation

$$\dot{A}'_\alpha = l'_{\alpha,\beta} A_\beta + \frac{1}{6} l'_{\alpha,\beta\gamma\delta} A_\beta A_\gamma A_\delta, \quad (6.1.93)$$

where

$$\begin{aligned} l'_{\alpha,\beta} &= -r_{\alpha\gamma}^{-1} d_{\gamma\beta}, \\ l'_{\alpha,\beta\gamma\delta} &= r_{\alpha\sigma}^{-1} f_{\sigma\beta\gamma\delta} - \frac{1}{3} (s_{\alpha\sigma\gamma\delta} d_{\sigma\beta} + s_{\alpha\beta\sigma\delta} d_{\sigma\gamma} + s_{\alpha\beta\gamma\sigma} d_{\sigma\delta}), \end{aligned} \quad (6.1.94)$$

is a special case of (4.3.9), the function being (4.3.33). Using the Markov FDRs (4.1.11) and (4.1.28), we find the fluctuational coefficients

$$l'_{\alpha\beta} = -2kT g_{\alpha\beta}^+ l'_{\alpha,\beta}, \quad (6.1.95)$$

$$l'_{\alpha\beta,\gamma\delta} = kT (-l'_{\alpha,\beta\gamma\delta} - l'_{\beta,\alpha\gamma\delta} + c_{\alpha\beta,\gamma\delta}), \quad (6.1.96)$$

where $c_{\alpha\beta,\gamma\delta}$ is the dissipationally undeterminable matrix having the property (4.1.27) and symmetry in subscripts α and β (also in γ and δ). Using (4.3.37) we can now deduce the coefficient of the master equation

$$K_{\alpha\beta}(B') = l'_{\alpha\beta} + \frac{1}{2} kT (-l'_{\alpha,\beta\gamma\delta} - l'_{\beta,\alpha\gamma\delta} + c_{\alpha\beta,\gamma\delta}) B_\gamma B_\delta. \quad (6.1.97)$$

Strictly speaking, according to (4.3.37), instead of $B_\gamma B_\delta$ we should have written $B_\gamma B_\delta - kT \partial B_\gamma / \partial B'_\delta$. However, the second term is relatively small, and so we ignore it.

Let us now write the stochastic equation [see Appendix A7, equation (A7.3)] corresponding to (6.1.93). Neglecting (since noise is small) the difference between the symmetrized stochastic equation and the Ito-type equation, we will have

$$\dot{B}'_\alpha = l'_{\alpha,\beta} B_\beta + \frac{1}{6} l'_{\alpha,\beta\gamma\delta} B_\beta B_\gamma B_\delta + \sum_s \sigma_\alpha^{(s)}(B) \xi^{(s)} \quad (6.1.98)$$

and, by (A7.5),

$$K_{\alpha\beta}(B) = \sum_s D_2^{(s)} \sigma_\alpha^{(s)}(B) \sigma_\beta^{(s)}(B) . \quad (6.1.99)$$

Proceeding in (6.1.98), as we proceeded from (6.1.81) to (6.1.82), we get

$$\begin{aligned} r_{\alpha\beta}^{-1}(p\delta_{\beta\gamma} + d_{\beta\gamma}) \tilde{J}_\gamma - \frac{1}{6} r_{\alpha\sigma}^{-1} f_{\sigma\beta\gamma\delta} \tilde{J}_\beta \tilde{J}_\gamma \tilde{J}_\delta + \frac{1}{6} s_{\alpha\sigma\gamma\delta} (p\delta_{\alpha\beta} + d_{\alpha\beta}) \tilde{J}_\beta \tilde{J}_\gamma \tilde{J}_\delta \\ = \sum_s \sigma_\alpha^{(s)}(\tilde{J}) \xi^{(s)} \end{aligned} \quad (6.1.100)$$

or, if we allow for (6.1.83),

$$\tilde{Z}_{1,2} \tilde{J}_2 + \frac{1}{6} \tilde{Z}_{1,234} \tilde{J}_2 \tilde{J}_3 \tilde{J}_4 = \sum_s \sigma_{\alpha_1}^{(s)}(\tilde{J}) \xi^{(s)}(t_1) . \quad (6.1.101)$$

This equation is nothing but (5.7.4), i.e. the equation

$$\mathcal{E}_1 + h_1 = Z_{1,2} J_2 + \frac{1}{6} Z_{1,234} J_2 J_3 J_4 \quad (6.1.102)$$

taken at zero external forces. Accordingly, the stochastic forces \mathcal{E} which appear in (5.7.4) are here

$$\mathcal{E}_\alpha(t) = \sum_s \sigma_\alpha^{(s)}(\tilde{J}) \xi^{(s)}(t) . \quad (6.1.103)$$

Assuming now \tilde{J} and $\xi^{(s)}$ to be statistically independent, i.e. examining (6.1.103) before it is substituted into (6.1.102), we can find the correlators (5.6.99), i.e. we can work out the functions $Z_{1,\dots,m,\dots}$. Specifically, making allowances for (6.1.99) gives

$$\langle \mathcal{E}_1, \mathcal{E}_2 \rangle_{\tilde{J}} = K_{\alpha_1 \alpha_2}(\tilde{J}) = \tilde{Z}_{12} + \frac{1}{6} \tilde{Z}_{12,34} \tilde{J}_3 \tilde{J}_4 . \quad (6.1.104)$$

Substituting (6.1.97) and using (6.1.94), we get

$$\begin{aligned} \beta \tilde{Z}_{\alpha\beta,\gamma\delta}(t_1, t_2, t_3, t_4) \\ = (-l'_{\alpha,\beta\gamma\delta} - l'_{\beta,\alpha\gamma\delta} + c_{\alpha\beta,\gamma\delta}) \delta(t_1, t_2, t_3, t_4) \\ = [-r_{\alpha\sigma}^{-1} f_{\sigma\beta\gamma\delta} - r_{\beta\sigma}^{-1} f_{\sigma\alpha\gamma\delta} + \frac{1}{3} (s_{\alpha\sigma\gamma\beta} d_{\sigma\delta} + s_{\beta\sigma\gamma\delta} d_{\sigma\alpha} \\ + 2s_{\alpha\beta\sigma\delta} d_{\sigma\gamma} + 2s_{\alpha\beta\gamma\sigma} d_{\sigma\delta}) + c_{\alpha\beta,\gamma\delta}] \delta(t_1, t_2, t_3, t_4) \end{aligned} \quad (6.1.105)$$

or, in the spectral form,

$$\begin{aligned} \beta \tilde{Z}_{12,34} = (2\pi)^{-1} [-P_{12} r_{\alpha_1\sigma}^{-1} f_{\sigma\alpha_2\alpha_3\alpha_4} + \frac{1}{3} (P_{12} s_{\alpha_1\sigma\alpha_3\alpha_4} d_{\sigma\alpha_2} \\ + 2P_{34} s_{\alpha_1\alpha_2\sigma\alpha_4} d_{\sigma\alpha_3}) + c_{\alpha\beta,\gamma\delta}] \delta(\omega_1 + \dots + \omega_4) . \end{aligned} \quad (6.1.106)$$

We will now use the equality $Z_{12,34}^{(2)} = Z_{1234} - Z_{1234}^{(1)}$, which by virtue of (5.7.55a) is equivalent to

$$\beta Z_{12,34}^{(2)} = \beta Z_{12,34} - Z_{1,234} - Z_{2,134} . \quad (6.1.107)$$

From this and (6.1.84), we will have

$$\begin{aligned}\beta \tilde{Z}_{12,34}^{(2)} &= (2\pi)^{-1} [c_{\alpha\beta,\gamma\delta} - \frac{1}{3}s_{1234}(i\omega_1 + i\omega_2 + 2i\omega_3 + 2i\omega_4)] \\ &\quad \times \delta(\omega_1 + \dots + \omega_4) \\ &= (2\pi)^{-1} [c_{\alpha\beta,\gamma\delta} + \frac{1}{6}s_{1234}(i\omega_1 + i\omega_2 - i\omega_3 - i\omega_4)] \\ &\quad \times \delta(\omega_1 + \dots + \omega_4).\end{aligned}\quad (6.1.108)$$

It can be readily verified that the last expression can be written as

$$\begin{aligned}\beta \tilde{Z}_{12,34}^{(2)} &= (2\pi)^{-1} [q_{\alpha_1\alpha_2\alpha_3\alpha_4} - \frac{1}{6}P_{12}r_{\alpha_2\beta}^{-1}(-i\omega_2\delta_{\beta\gamma} + d_{\beta\gamma})r_{\gamma\delta}s_{\alpha_1\delta\alpha_3\alpha_4} \\ &\quad - \frac{1}{6}P_{34}S_{\alpha_1\alpha_2\beta\alpha_4}(i\omega_3\delta_{\beta\alpha_3} + d_{\beta\alpha_3})] \delta(\omega_1 + \dots + \omega_4),\end{aligned}\quad (6.1.109)$$

where

$$q_{\alpha_1\alpha_2\alpha_3\alpha_4} = c_{\alpha_1\alpha_2,\alpha_3\alpha_4} + \frac{1}{6}(P_{12}r_{\alpha_2\beta}^{-1}d_{\beta\gamma}r_{\gamma\delta}s_{\alpha_1\delta\alpha_3\alpha_4} + P_{34}s_{\alpha_1\alpha_2\beta\alpha_4}d_{\beta\alpha_3}). \quad (6.1.110)$$

According to (6.1.32a) and the equation $\varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma\varepsilon_\delta s_{\alpha\beta\gamma\delta} = s_{\alpha\beta\gamma\delta}$, the matrix (6.1.110) has the same symmetry properties as $c_{\alpha\beta,\gamma\delta}$; see (4.1.27). Considering this, we can easily show that (6.1.109) obeys (6.1.89).

Furthermore, using (6.1.109) we can obtain from (6.1.90)

$$\begin{aligned}\beta \tilde{Y}_{12,34}^{(2)} &= (2\pi)^{-1} [(i\omega_1 + \hat{D}_1)^{-1}\hat{R}_1(i\omega_2 + \hat{D}_2)^{-1}\hat{R}_2q_{1234}(-i\omega_3 + \hat{D}_3)^{-1}\hat{R}_3 \\ &\quad \times (-i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4 - \frac{1}{6}P_{12}(i\omega_1 + \hat{D}_1)^{-1}\hat{R}_1\hat{R}_2s_{1234} \\ &\quad \times (-i\omega_3 + \hat{D}_3)^{-1} \\ &\quad \times (\hat{R}_3(-i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4 - \frac{1}{6}P_{34}(i\omega_1 + \hat{D}_1)^{-1}\hat{R}_1 \\ &\quad \times (i\omega_2 + \hat{D}_2)^{-1} \\ &\quad \times \hat{R}_2s_{1234}\hat{R}_3(-i\omega_4 + \hat{D}_4)^{-1}\hat{R}_4] \delta(\omega_1 + \dots + \omega_4).\end{aligned}\quad (6.1.111)$$

We have thus found the desired functions.

6.1.6 Dissipationally Undeterminable Part of the Fourfold Correlator

Substituting (6.1.111) into the FDR (6.1.92), or rather into

$$\beta^2 \langle B_1, B_2, B_3, B_4 \rangle^{(2)} = P_{14}(P_{(234)} \hat{Y}_{12,34}^{(2)}), \quad (6.1.112)$$

we obtain the spectral representation for the dissipationally undeterminable part of the fourfold correlator. To find the total correlator we will have to add (6.1.87) to (6.1.112). From (6.1.87) and (6.1.111, 112) we will thus have, using the notation of (6.1.88),

$$\begin{aligned}
& \beta^3 \langle B_1, B_2, B_3, B_4 \rangle \\
&= (2\pi)^{-1} \left\{ P_{(1234)} [(\mathrm{i}\omega_1 + \hat{D}_1)^{-1} f_{1234} (-\mathrm{i}\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 \right. \\
&\quad \times (-\mathrm{i}\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 (-\mathrm{i}\omega_4 + \hat{D}_4)^{-1} \hat{R}_4 \\
&\quad + \varepsilon_1 \varepsilon_2 \varepsilon_3 \varepsilon_4 (-\mathrm{i}\omega_1 + \hat{D}_1)^{-1} f_{1234} (\mathrm{i}\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 \\
&\quad \times (\mathrm{i}\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 (\mathrm{i}\omega_4 + \hat{D}_4)^{-1} R_4 \\
&\quad \left. - \frac{1}{2} P_{(234)} (N_{1234} + \bar{N}_{4321})] \right. \\
&+ P_{14} [P_{(234)} (\mathrm{i}\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 (\mathrm{i}\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 q_{1234} \\
&\quad \times (-\mathrm{i}\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 (-\mathrm{i}\omega_4 + \hat{D}_4)^{-1} \hat{R}_4] \} \delta(\omega_1 + \dots + \omega_4). \quad (6.1.113)
\end{aligned}$$

From the spectral representation we can transfer to the temporal representation

$$\begin{aligned}
& \beta^3 \langle B_1, B_2, B_3, B_4 \rangle \\
&= P_{(1234)} \left\{ \int \hat{V}_1(t_{10}) f_{1234} \hat{V}_2(t_{02}) \hat{R}_2 \hat{V}_3(t_{03}) \hat{R}_3 \hat{V}_4(t_{04}) \hat{R}_4 dt_0 \right. \\
&\quad + \varepsilon_1 \varepsilon_2 \varepsilon_3 \varepsilon_4 \int \hat{V}_1(t_{01}) f_{1234} \hat{V}_2(t_{20}) \hat{R}_2 \hat{V}_3(t_{30}) \hat{R}_3 \hat{V}_4(t_{40}) \\
&\quad \times \hat{R}_4 dt_0 - \frac{1}{2} P_{(234)} (M_{1234} + \bar{M}_{4321}) \left. \right\} \\
&+ P_{14} \left\{ P_{(234)} \int \hat{V}_1(t_{10}) \hat{R}_1 \hat{V}_2(t_{20}) \hat{R}_2 q_{1234} \hat{V}_3(t_{03}) \hat{R}_3 \hat{V}_4(t_{04}) \hat{R}_4 dt_0 \right\}, \quad (6.1.114)
\end{aligned}$$

where

$$\hat{M}_{1234} = \hat{V}_1(t_{12}) \hat{R}_1 \hat{R}_2 s_{1234} \hat{V}_3(t_{23}) \hat{R}_3 \hat{V}_4(t_{24}) \hat{R}_4, \quad (6.1.115)$$

$$\bar{M}_{4321} = M_{1234}^{tc} = \hat{V}_4(t_{42}) \hat{R}_4 \hat{V}_3(t_{32}) \hat{R}_3 s_{4321} \hat{R}_2 \hat{V}_1(t_{21}) \hat{R}_1. \quad (6.1.116)$$

The expression for the correlator will contain fewer terms if we confine ourselves to the region $t_1 > t_2 > t_3 > t_4$. Examining the “spheres of influence” of some terms in (6.1.114) we can easily obtain

$$\begin{aligned}
& \beta^3 \langle B_1, B_2, B_3, B_4 \rangle \\
&= \int \hat{V}_1(t_{10}) f_{1234} \hat{V}_2(t_{02}) \hat{R}_2 \hat{V}_3(t_{03}) \hat{R}_3 \hat{V}_4(t_{04}) \hat{R}_4 dt_0 \\
&\quad + \varepsilon_1 \varepsilon_2 \varepsilon_3 \varepsilon_4 \int \hat{V}_4(t_{04}) f_{4321} \hat{V}_3(t_{30}) \hat{R}_3 \hat{V}_2(t_{20}) \hat{R}_2 \hat{V}_1(t_{10}) \hat{R}_1 dt_0 \\
&\quad - \frac{1}{2} (M_{1234} + \bar{M}_{1234}) \\
&\quad + \int \hat{V}_1(t_{10}) \hat{R}_1 \hat{V}_2(t_{20}) \hat{R}_2 q_{1234} \hat{V}_3(t_{03}) \hat{R}_3 \hat{V}_4(t_{04}) \hat{R}_4 dt_0, \\
&\quad \text{for } t_1 > t_2 > t_3 > t_4. \quad (6.1.117)
\end{aligned}$$

In the first term, integration with respect to t_0 is between t_2 and t_1 , in the second term between t_4 and t_3 , and in the third term between t_3 and t_2 . This integration can be carried out using the technique applied in Sect. 6.1.2 [see (6.1.45, 46)] to yield

$$\begin{aligned} & \beta^3 \langle B_1, B_2, B_3, B_4 \rangle \\ &= H_{\alpha_1 \lambda \mu \nu}(t_1, t_2, t_3, t_4) r_{\lambda \alpha_2} r_{\mu \alpha_3} r_{\nu \alpha_4} \\ &+ \varepsilon_1 \varepsilon_2 \varepsilon_3 \varepsilon_4 H_{\alpha_4 \lambda \mu \nu}(-t_4, -t_3, -t_2, -t_1) r_{\lambda \alpha_3} r_{\mu \alpha_2} r_{\nu \alpha_1} \\ &+ H'_{\alpha_1 \alpha_2 \mu \nu}(t_1, t_2, t_3, t_4) r_{\mu \alpha_3} r_{\nu \alpha_4} \\ &- \frac{1}{2} [\hat{V}(t_{12}) \hat{R}]_{\alpha_1 \mu} r_{\alpha_2 \nu} s_{\mu \nu \rho \sigma} [\hat{V}(t_{23}) \hat{R}]_{\rho \alpha_3} [\hat{V}(t_{24}) \hat{R}]_{\sigma \alpha_4} \\ &- \frac{1}{2} [\hat{V}(t_{13}) \hat{R}]_{\alpha_1 \mu} [\hat{V}(t_{23}) \hat{R}]_{\alpha_2 \nu} s_{\mu \nu \rho \sigma} r_{\rho \alpha_3} [\hat{V}(t_{34}) \hat{R}]_{\sigma \alpha_4}, \\ & \text{for } t_1 > t_2 > t_3 > t_4, \end{aligned} \quad (6.1.118)$$

where

$$H_{1234} = m_{1234} \hat{V}_2(t_{12}) \hat{V}_3(t_{13}) \hat{V}_4(t_{14}) - \hat{V}_1(t_{12}) m_{1234} \hat{V}_3(t_{23}) \hat{V}_4(t_{24}), \quad (6.1.119a)$$

$$H'_{1234} = \hat{V}_1(t_{12}) m'_{1234} \hat{V}_3(t_{23}) \hat{V}_4(t_{24}) - \hat{V}_1(t_{13}) \hat{V}_2(t_{23}) m'_{1234} \hat{V}_4(t_{34}). \quad (6.1.119b)$$

The matrices m_{1234} and m'_{1234} are given by

$$d_{\alpha \sigma} m_{\alpha \beta \gamma \delta} - m_{\alpha \sigma \gamma \delta} d_{\alpha \beta} - m_{\alpha \beta \sigma \delta} d_{\alpha \gamma} - m_{\alpha \beta \gamma \sigma} d_{\alpha \delta} = f_{\alpha \beta \gamma \delta} \quad (6.1.120a)$$

$$d_{\alpha \sigma} m'_{\alpha \beta \gamma \delta} + d_{\beta \sigma} m'_{\alpha \sigma \gamma \delta} - m'_{\alpha \beta \sigma \delta} d_{\alpha \gamma} - m'_{\alpha \beta \gamma \sigma} d_{\alpha \delta} = r_{\alpha \rho} r_{\beta \sigma} q_{\rho \sigma \gamma \delta}. \quad (6.1.120b)$$

The result (6.1.118) can also be derived from the master equation.

6.1.7 Four-Subscript Derivatives of Correlators with Respect to Forces

To begin with, we will consider the derivative

$$\begin{aligned} \delta^2 \langle B_1, B_2 \rangle / \delta \tilde{h}_3 \delta \tilde{h}_4 |_{\tilde{h}=0} &= \tilde{Y}_{12,34} \\ &= \tilde{Y}_{12,34}^{(1)} + \tilde{Y}_{12,34}^{(2)}. \end{aligned} \quad (6.1.121)$$

Using (5.4.109a) and (6.1.86, 111), we obtain

$$\begin{aligned} \beta \tilde{Y}_{12,34} &= (2\pi)^{-1} \{ P_{12} [(i\omega_1 + \hat{D}_1)^{-1} f_{1234} (-i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 \\ &\times (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 (-i\omega_4 + \hat{D}_4)^{-1} \hat{R}_4] + (i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 \\ &\times (i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 q_{1234} (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 (-i\omega_4 + \hat{D}_4)^{-1} \hat{R}_4 \\ &- \frac{1}{2} P_{12} N_{1234} - \frac{1}{3} P_{12} (N_{1342} + N_{1432}) \\ &- \frac{1}{6} P_{34} \bar{N}_{1234} \} \delta(\omega_1 + \omega_2 + \omega_3 + \omega_4). \end{aligned} \quad (6.1.122)$$

We will now give the temporal version corresponding to (6.1.122). We confine

ourselves to the expression for the ordered times

$$\begin{aligned} \beta \tilde{Y}_{12,34} &= H_{1234} \hat{R}_2 \hat{R}_3 \hat{R}_4 + H'_{1234} \hat{R}_3 \hat{R}_4 \\ &\quad - \frac{1}{2} \hat{V}_1(t_{12}) \hat{R}_1 \hat{R}_2 s_{1234} \hat{V}_3(t_{23}) \hat{R}_3 \hat{V}_4(t_{24}) \hat{R}_4 \\ &\quad - \frac{1}{3} \hat{V}_1(t_{13}) \hat{R}_1 \hat{R}_3 s_{1234} \hat{V}_2(t_{32}) \hat{R}_2 \hat{V}_4(t_{34}) \hat{R}_4 \\ &\quad - \frac{1}{6} \hat{V}_1(t_{13}) \hat{R}_1 \hat{V}_2(t_{23}) \hat{R}_2 s_{1234} \hat{R}_3 \hat{V}_4(t_{34}) \hat{R}_4, \\ \text{for } t_1 > t_2, t_3 > t_4. \end{aligned} \quad (6.1.123)$$

The first terms are given by (6.1.119).

Let us now consider the derivative of the threefold correlator

$$\begin{aligned} \delta \langle B_1, B_2, B_3 \rangle / \delta \tilde{h}_4 |_{\tilde{h}=0} &= \tilde{Y}_{123,4} \\ &= \tilde{Y}_{123,4}^{(1)} + \tilde{Y}_{123,4}^{(2)}. \end{aligned} \quad (6.1.124)$$

According to (5.4.108b, 109b) we have

$$\begin{aligned} Y_{123,4} &= Y_{123,4}^{(1)} + Y_{123,4}^{(2)} \\ &= (kT)^2 (Y_{4,123}^{\text{c}} + P_{(123)} Y_{1,234}) + kTP_{(123)} Y_{12,34}^{(2)}. \end{aligned} \quad (6.1.125)$$

Therefore, using (6.1.86) and (6.1.111), we obtain

$$\begin{aligned} \beta^2 \tilde{Y}_{123,4} &= (2\pi)^{-1} \{ P_{(123)} (i\omega_1 + \hat{D}_1)^{-1} f_{1234} (-i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 \\ &\quad \times (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 (-i\omega_4 + \hat{D}_4)^{-1} \hat{R}_4 \\ &\quad + \varepsilon_1 \varepsilon_2 \varepsilon_3 \varepsilon_4 (-i\omega_4 + \hat{D}_4)^{-1} f_{4123} (i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 \\ &\quad \times (i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 (i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 \\ &\quad + P_{(123)} (i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1 (i\omega_2 + \hat{D}_2)^{-1} \hat{R}_2 q_{1234} \\ &\quad \times (-i\omega_3 + \hat{D}_3)^{-1} \hat{R}_3 (-i\omega_4 + \hat{D}_4)^{-1} \hat{R}_4 - \frac{1}{2} P_{123} N_{1234} \\ &\quad - \frac{1}{3} P_{(123)} N_{1423} - \frac{1}{2} P_{(123)} \bar{N}_{1234} \\ &\quad - \frac{1}{6} P_{(123)} \bar{N}_{1243} \} \delta(\omega_1 + \dots + \omega_4). \end{aligned} \quad (6.1.126)$$

Consequently, in the time representation, for $t_1 > t_2 > t_3 > t_4$ we will have

$$\begin{aligned} \beta^2 \tilde{Y}_{123,4} &= H_{\alpha_1 \lambda \mu \nu}(t_1, t_2, t_3, t_4) r_{\lambda \alpha_2} r_{\mu \alpha_3} r_{\nu \alpha_4} \\ &\quad + \varepsilon_{\alpha_1} \dots \varepsilon_{\alpha_4} H_{\alpha_4 \lambda \mu \nu}(-t_4, -t_1, -t_2, -t_3) r_{\lambda \alpha_1} r_{\mu \alpha_2} r_{\nu \alpha_3} \\ &\quad + H'_{\alpha_1 \alpha_2 \mu \nu}(t_1, t_2, t_3, t_4) r_{\mu \alpha_3} r_{\nu \alpha_4} \\ &\quad - \frac{1}{2} M_{1234} - \frac{1}{3} M_{1423} - \frac{1}{2} \bar{M}_{1234} - \frac{1}{6} \bar{M}_{1243}. \end{aligned} \quad (6.1.127)$$

All the four-subscript functions are thus expressed through the dissipationally determinable matrix $f_{\alpha \beta \gamma \delta}$ and the dissipationally undeterminable matrix $q_{\alpha \beta \gamma \delta}$. For the latter to be found in specific cases, we will have to construct a theoretical model of a fluctuation-dissipational process or perform a partial experimental study of the behaviour of one of the functions (6.1.118), (6.1.123), (6.1.127) or appropriate spectral functions.

Symmetry, if any, of one system or another enables one to reduce the number of dissipationally undeterminable parameters. In addition, this number is further reduced drastically if the number of dissipative terms in the phenomenological equation is much smaller than the number of components of the vector of parameters. Examples of these reductions will be given below.

6.2 Examples of Computations of Many-Fold Correlators or Spectral Densities and Their Derivatives with Respect to External Forces

6.2.1 A Nonlinear Resistance–Inductance Electrical Circuit

By way of example, consider a simple circuit (Fig. 6.1) consisting of an inductance and a nonlinear resistance. The circuit is similar to one discussed in Sect. 4.4.2 where the inductance is now taken to be nonlinear. Let its energy as a function of current be

$$W(I) = \frac{1}{2}LI^2 + \frac{1}{6}sI^3. \quad (6.2.1)$$

At $A_1 = I$ in this example the above relationship is a specific case of the formula (6.1.2). Using (6.1.55) by the expression

$$p = LI + \frac{1}{4}sI^2, \quad (6.2.2)$$

we introduce the new variable $A'_1 = p$, “momentum”, that here replaces I . Now the formula

$$dW[I(p)]/dp = I \quad (6.2.3)$$

holds [see (6.1.51)], and the derivative $\dot{p} = dp/dt$ has the sense of the e.m.f. across the inductance. Suppose that in the circuit under consideration there acts an external e.m.f. \tilde{h} connected in series. The balance of voltages is given by

$$\dot{p} + V(I) = \tilde{h}, \quad (6.2.4)$$

where $V(I)$ is the voltage across the nonlinear resistance according to (4.5.14). Substituting (4.5.14) into (6.2.4) gives

$$\dot{p} + RI + \frac{1}{2}\alpha I^2 = \tilde{h}. \quad (6.2.5)$$

This is a particular case of (6.1.61). If we substitute (6.2.2) into (6.2.5), we will obtain (6.1.64). Comparison of (6.2.1) with (6.1.2) shows that here the matrices $r_{\alpha\beta}$ and $s_{\alpha\beta\gamma}$

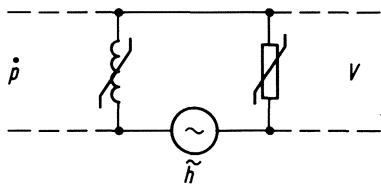


Fig. 6.1. Example of a circuit with a nonlinear resistor

have the form

$$\begin{aligned} r_{11} &= 1/L, \\ s_{111} &= s. \end{aligned} \tag{6.2.6}$$

Furthermore, comparison of (6.2.5) with (6.1.61) gives

$$\begin{aligned} r_{11}^{-1} d_{11} &= R, \\ r_{11}^{-1} f_{111} - s_{111} d_{11} &= -\alpha, \end{aligned} \tag{6.2.7}$$

i.e. in this case,

$$\begin{aligned} d_{11} &= R/L \equiv \gamma, \\ f_{111} &= (sR/L - \alpha)/L. \end{aligned} \tag{6.2.8}$$

The values (6.2.6) and (6.2.8) can be substituted into the one-component version of (6.1.41), i.e. (since here $\varepsilon_1 = -1$) into

$$\begin{aligned} \beta^2 \langle I_1, I_2, I_3 \rangle &= (2\pi)^{-1/2} \{ P_{(123)} [(\mathrm{i}\omega_1 + d_{11})^{-1} f_{111} (-\mathrm{i}\omega_2 + d_{11})^{-1} (-\mathrm{i}\omega_3 + d_{11})^{-1} r_{11}^2 \\ &\quad - (-\mathrm{i}\omega_1 + d_{11})^{-1} f_{111} (\mathrm{i}\omega_2 + d_{11})^{-1} \\ &\quad \times (\mathrm{i}\omega_3 + d_{11})^{-1} r_{11}^2] \\ &\quad - P_{123} [(\mathrm{i}\omega_1 + d_{11})^{-1} s_{111} (-\mathrm{i}\omega_3 + d_{11})^{-1} r_{11}^3] \} \delta(\omega_1 + \omega_2 + \omega_3). \end{aligned} \tag{6.2.9}$$

This gives the threefold correlator in the spectral form. In addition, by using (6.1.47, 48) and (6.1.50) we can obtain the correlator in the temporal form

$$\begin{aligned} \beta^2 \langle I_1, I_2, I_3 \rangle &= \frac{m_{111}}{L^2} \exp(-\gamma t_{13}) [\exp(-\gamma t_{12}) - \exp(-\gamma t_{23})] \\ &\quad - \frac{s}{L^3} \exp(-\gamma t_{13}) \end{aligned} \tag{6.2.10}$$

for $t_1 > t_2 > t_3$, where

$$m_{111} = -f_{111}/d = \alpha/R - s/L.$$

Furthermore, using (6.1.76) we can readily find

$$\begin{aligned} \frac{\delta \langle I(\omega_1), I(\omega_2) \rangle}{\delta h(\omega_3)} &= kT (2\pi)^{-1/2} \left\{ \frac{f_{111}}{L^2} [P_{12} (\mathrm{i}\omega_1 + \gamma)^{-1} (-\mathrm{i}\omega_2 + \gamma)^{-1} (-\mathrm{i}\omega_3 + \gamma)^{-1} \right. \\ &\quad \left. - (\mathrm{i}\omega_1 + \gamma)^{-1} (\mathrm{i}\omega_2 + \gamma)^{-1} (-\mathrm{i}\omega_3 + \gamma)^{-1}] \right. \\ &\quad \left. - \frac{s_{111}}{2L^3} P_{12} [2(\mathrm{i}\omega_1 + \gamma)^{-1} (-\mathrm{i}\omega_3 + \gamma)^{-1} \right. \\ &\quad \left. + (\mathrm{i}\omega_1 + \gamma)^{-1} (-\mathrm{i}\omega_2 + \gamma)^{-1}] \right\} \delta(\omega_1 + \omega_2 + \omega_3). \end{aligned} \tag{6.2.11}$$

If then we use this result and the equation

$$\langle I(\omega_1), I(\omega_2) \rangle_0 = \frac{2kTR}{L^2} (\omega_1^2 + \gamma^2)^{-1} \delta(\omega_1 + \omega_2) \quad (6.2.12)$$

derivable, for example, from (6.1.25), we can write the total nonequilibrium correlator in a linear-quadratic approximation

$$\begin{aligned} & \langle I(\omega_1), I(\omega_2) \rangle \\ &= 2kTRL^{-2} (\omega_1^2 + \gamma^2) \delta(\omega_1 + \omega_2) + \int \frac{\delta \langle I(\omega_1), I(\omega_2) \rangle}{\delta h(\omega_3)} h(\omega_3) d\omega_3, \end{aligned} \quad (6.2.13)$$

where

$$h(\omega) = (2\pi)^{-1/2} \int \exp(i\omega t) h(t) dt. \quad (6.2.14)$$

In particular, if we take a constant external e.m.f. $h(t) = u_0$, which by (6.2.14) gives $h(\omega) = (2\pi)^{1/2} u_0 \delta(\omega)$, then from (6.2.11–13) we get

$$\begin{aligned} \langle I(\omega_1), I(\omega_2) \rangle &= kT \{ 2L^{-2} R(\omega_1^2 + \gamma^2)^{-1} \\ &\quad + \gamma^{-1} L^{-2} f_{111} u_0 [2\text{Re}(i\omega_1 + \gamma)^{-2} - (\omega_1^2 + \gamma^2)^{-1}] \\ &\quad - L^{-3} s_{111} u_0 [2(\omega_1^2 + \gamma^2)^{-1} \\ &\quad + \text{Re}(i\omega_1 + \gamma)^{-2}] \} \delta(\omega_1 + \omega_2). \end{aligned} \quad (6.2.15)$$

We have thus found the nonequilibrium spectral density corresponding to the action of a constant e.m.f.

It is worth noting that a quantum generalization of (6.2.9) and (6.2.11) can also be obtained in a fairly simple manner. So, from the FDR (5.3.98a) we find the symmetrized quantum moment

$$\begin{aligned} \frac{1}{4} \langle [[I(\omega_1), I(\omega_2)]_+, I(\omega_3)]_+ \rangle &= P_{12} \Theta(i\omega_2) \Theta(i\omega_3) W_{123} \\ &\quad + \frac{1}{2} [\Theta^+(i\omega_1) \Theta^+(i\omega_2) \\ &\quad + \Theta^+(-i\omega_1) \Theta^+(-i\omega_2)] W_{312}, \end{aligned} \quad (6.2.16)$$

where

$$\begin{aligned} W_{123} &= (2\pi)^{-1/2} (kT)^2 L^{-3} i \text{Im} [2L f_{111} (i\omega_1 + \gamma)^{-1} (-i\omega_2 + \gamma)^{-1} \\ &\quad \times (-i\omega_3 + \gamma)^{-1} - s P_{23} (i\omega_1 + \gamma)^{-1} \\ &\quad \times (-i\omega_2 + \gamma)^{-1}] \delta(\omega_1 + \omega_2 + \omega_3), \end{aligned} \quad (6.2.17a)$$

$$\begin{aligned} 2\Theta(i\omega) &= \Theta^+(i\omega) + \Theta^+(-i\omega) \\ &= \beta\hbar\omega \coth(\frac{1}{2}\beta\hbar\omega). \end{aligned} \quad (6.2.17b)$$

The functions $\Theta^\pm(i\omega)$ are given by (5.2.74, 79) and (5.3.93).

6.2.2 An Electrical Circuit with Capacitance and Cubic Nonlinear Resistance

Let us now return to the case considered in Sect. 4.5.5 where the role of the internal parameter A_1 is played by a time-even parameter – the charge Q on the capacitance C . Assuming a linear capacitance, we have the energy $F = W = Q^2/(2C)$. Therefore,

$$\begin{aligned} r_{11} &= C, \\ s_{111} &= 0. \end{aligned} \tag{6.2.18}$$

With the current–voltage characteristic (4.5.63) the phenomenological relaxation equation has the form (4.5.64). Comparing it with (6.1.77) gives

$$\begin{aligned} d_{11} &= S/C \equiv \gamma, \\ f_{1111} &= -\lambda/C^3. \end{aligned} \tag{6.2.19}$$

With (6.2.18, 19) taken into account, we can use the one-component form of (6.1.118) to determine the fourfold correlator in the time representation

$$\begin{aligned} \beta^3 \langle Q(t_1), \dots, Q(t_4) \rangle &= -\frac{C^3 f_{1111}}{2\gamma} \{ \exp[-\gamma(t_{12} + t_{13} + t_{14})] \\ &\quad + \exp[-\gamma(t_{14} + t_{24} + t_{34})] \\ &\quad - 2\exp[-\gamma(t_{13} + t_{24})] \} \\ &\quad + c_0 t_{23} \exp[-\gamma(t_{13} + t_{24})] \end{aligned} \tag{6.2.20}$$

for $t_1 > t_2 > t_3 > t_4$. Here $c_0 = C^4 q_{1111}$ is a dissipationally undeterminable parameter. We cannot compute the last term on the right-hand side of (6.2.20) by using (6.1.120b) since its left-hand side vanishes, just as the expression on the right-hand side of (6.1.119b) does. This occurs because the integrand in the appropriate term in (6.1.117) is independent of t_0 . Integration here is a trivial exercise, as it reduces to multiplication by the integration interval.

It is seen from (6.2.20) that the term with a dissipationally undeterminable parameter has a different behaviour from the other terms. In particular, it follows from (6.2.20) that

$$\langle Q(t_1), Q(t_1), Q(t_2), Q(t_2) \rangle = (kT)^3 c_0 t_{12} \exp(-2\gamma t_{12}), \quad t_{12} > 0. \tag{6.2.21}$$

It is easily seen that the two-time correlator $\langle Q^2(t_1), Q^2(t_2) \rangle$, which is proportional to the energy correlator, is

$$\langle Q^2(t_1), Q^2(t_2) \rangle = 2\langle Q(t_1), Q(t_2) \rangle^2 + \langle Q(t_1), Q(t_1), Q(t_2), Q(t_2) \rangle. \tag{6.2.22}$$

This suggests that the dissipationally undeterminable parameter c_0 can be found experimentally by analysing the difference of (6.2.22) from the expression

$$2\langle Q(t_1), Q(t_2) \rangle^2 = 2(kTC)^2 \exp(-2\gamma t_{12}), \quad t_{12} > 0, \tag{6.2.23}$$

which is obtained using the linear theory.

6.2.3 The Threefold Correlator of the Internal Energy of a Body in Thermal Contact with Another Body

We will now continue the discussion of the weakly nonlinear heat exchange of two bodies thermally isolated from other bodies (Sect. 4.5.3). To simplify our reasoning we will make a weak assumption that the heat capacities c_1 and c_2 of the bodies are temperature-independent. Using (4.5.33, 43) we can then reduce (4.5.34) to the form

$$\dot{U}_1 = -\lambda \frac{c_1 + c_2}{c_1 c_2} (U_1 - U_1^0) - \mu \left(\frac{c_1 + c_2}{c_1 c_2} \right)^2 (U_1 - U_1^0)^2. \quad (6.2.24)$$

Equating $U_1 - U_1^0$ to A_1 and comparing (6.2.24) with the equality

$$\dot{A}_\alpha = -d_{\alpha\beta} A_\beta + \frac{1}{2} f_{\alpha\beta\gamma} A_\beta A_\gamma, \quad (6.2.25)$$

which is equivalent to (6.1.1), we obtain

$$\begin{aligned} d_{11} &\equiv \gamma = \lambda(c_1 + c_2)/(c_1 c_2), \\ f_{111} &= -2\mu(c_1 + c_2)^2/(c_1 c_2)^2. \end{aligned} \quad (6.2.26)$$

From (4.5.30, 36) we have

$$\begin{aligned} dS &= -X dU_1 \\ &= -\Theta^{-3} \left[(T_1 - T_2)\Theta + \frac{c_1 - c_2}{c_1 + c_2} (T_1 - T_2)^2 \right] dU_1 \end{aligned} \quad (6.2.27)$$

or, using (4.5.33, 43),

$$-dS = \Theta^{-3} \frac{c_1 + c_2}{c_1 c_2} \left[(U_1 - U_1^0)\Theta + \frac{c_1 - c_2}{c_1 c_2} (U_1 - U_1^0)^2 \right] dU_1. \quad (6.2.28)$$

Integrating this gives

$$-S = \Theta^{-3} \frac{c_1 + c_2}{c_1 c_2} \left[\frac{\Theta}{2} (U_1 - U_1^0)^2 + \frac{c_1 - c_2}{3c_1 c_2} (U_1 - U_1^0)^3 \right] + \text{const.} \quad (6.2.29)$$

In the given example we should utilize the modified form of nonequilibrium thermodynamics, which is based on entropy and not on free energy. In doing so, instead of (6.1.2) we should take the equation

$$-S(A) = \frac{1}{2} r_{\alpha\beta}^{-1} A_\alpha A_\beta + \frac{1}{6} s_{\alpha\beta\gamma} A_\alpha A_\beta A_\gamma + \text{const.} \quad (6.2.30)$$

and in (6.1.41) and other formulas we should substitute k^{-1} for $\beta = (kT)^{-1}$. Comparing (6.2.29) with (6.2.30), we obtain

$$\begin{aligned} r_{11} &= \Theta^2 \frac{c_1 c_2}{c_1 + c_2}, \\ {}^*s_{111} &= 2\Theta^{-3} \frac{c_1^2 - c_2^2}{c_1^2 c_2^2}. \end{aligned} \quad (6.2.31)$$

After having found the values (6.2.26) and (6.2.31) from (6.1.47–49) with k^{-1} substituted for β (Sects. 5.3.8, 9) we can find the three-time correlator

$$\begin{aligned} \langle U_1(t_1), U_1(t_2), U_1(t_3) \rangle = & -k^2 \Theta^4 \left(\frac{c_1 c_1}{c_1 + c_2} \right)^2 \frac{f_{111}}{\lambda} \{ 2 \exp(-\gamma t_{13}) \} \\ & - \exp[-\gamma(t_{12} + t_{13})] - \exp[-\gamma(t_{13} + t_{23})] \} \\ & - k^2 \Theta^6 \left(\frac{c_1 c_2}{c_1 + c_2} \right)^3 s_{111} \exp(-\gamma t_{13}) \end{aligned} \quad (6.2.32)$$

for $t_1 > t_2 > t_3$. The fact that this correlator is nonzero is due either to the heat capacities c_1 and c_2 being different or to the heat exchange (4.5.29) being asymmetric. The latter property is described by

$$df(T_1, T_2)/\partial T_1 \neq df(T_1, T_2)/\partial T_2$$

[see (4.5.35)], so that $\mu \neq 0$ even at $c_1 = c_2$.

6.2.4 Velocity Correlators of a Body Travelling with Nonlinear Friction in an Isotropic Medium

We would now like to compute the correlators for the mechanical example discussed earlier in Sect. 4.5.7. Let the internal parameters A_1, A_2, A_3 be the components of the velocity v , and the parameters (6.1.79) be the components p_α of the momentum. Equation (6.1.51) will then coincide with some of the Hamiltonian equations, namely with

$$\dot{q}_\alpha \equiv v_\alpha = \partial \mathcal{H}(p)/\partial p_\alpha. \quad (6.2.33)$$

If the kinetic energy of a body has the conventional form $W = mv^2/2$, then $p_\alpha = mv_\alpha$, $\mathcal{H}(p) = \sum p_\alpha^2/2m$.

The derivatives \dot{p}_α have the sense of the components of the mechanical force conjugate to the coordinates of the body in question. The external force \tilde{h} is here coincident with the external mechanical force f . When it acts, we have, instead of (4.5.85), the equation

$$\dot{p}_\alpha = -\gamma v_\alpha - \lambda v^2 v_\alpha + f_\alpha(t), \quad (6.2.34)$$

which is an example of (6.1.81). Accordingly, in this case we have

$$\begin{aligned} r_{\alpha\beta} &= m^{-1} \delta_{\alpha\beta}, \\ d_{\alpha\beta} &= (\gamma/m) \delta_{\alpha\beta}, \\ s_{\alpha\beta\gamma\delta} &= 0, \end{aligned} \quad (6.2.35)$$

and the matrix $f_{\alpha\beta\gamma\delta}$ has the form

$$f_{\alpha\beta\gamma\sigma} = -2(\lambda/m)(\delta_{\alpha\beta}\delta_{\gamma\sigma} + \delta_{\alpha\gamma}\delta_{\beta\sigma} + \delta_{\alpha\sigma}\delta_{\beta\gamma}), \quad (6.2.36)$$

cf. (4.5.86b).

Let us now consider the dissipationally undeterminable matrix $q_{\alpha\beta\gamma\delta}$, which by (6.1.110) coincides with $c_{\alpha\beta\gamma\delta}$ and has the symmetry $q_{\alpha\beta\gamma\delta} = q_{\beta\alpha\gamma\delta} = q_{\alpha\beta\delta\gamma} = q_{\gamma\delta\alpha\beta}$. Using (4.5.90) we have

$$q_{\alpha\beta\gamma\sigma} = (c_{||} - c_{\perp})(\delta_{\alpha\gamma}\delta_{\beta\sigma} + \delta_{\alpha\sigma}\delta_{\beta\gamma}) + 2c_{\perp}\delta_{\alpha\beta}\delta_{\gamma\sigma}, \quad (6.2.37)$$

where, as noted in Sect. 4.5.7, the main contribution comes from the parameter $c_{||}$.

Knowing the matrices (6.2.35–37) and using the formulas from Sects. 6.1.6, 7 we can find the correlators for the velocities and their derivatives with respect to the forces.

Applying (6.1.122) to the above matrices gives

$$\begin{aligned} \frac{1}{2}\tilde{Y}_{12,34}f_3f_4 &= (4\pi)^{-1}kTm^{-4} \int \left\{ -2\lambda P_{12}(i\omega_1 + \gamma/m)^{-1} \right. \\ &\quad \times (-i\omega_2 + \gamma/m)^{-1}(-i\omega_3 + \gamma/m)^{-1} \\ &\quad \times (-i\omega_4 + \gamma/m)^{-1}[\delta_{\alpha_1\alpha_2}f_{\beta}(\omega_3)f_{\beta}(\omega_4) \\ &\quad + P_{34}f_{\alpha_1}(\omega_3)f_{\alpha_2}(\omega_4)] \\ &\quad + (i\omega_1 + \gamma/m)^{-1}(i\omega_2 + \gamma/m)^{-1} \\ &\quad \times (-i\omega_3 + \gamma/m)^{-1}(-i\omega_4 + \gamma/m)^{-1} \\ &\quad \times [2c_{\perp}\delta_{\alpha_1\alpha_2}f_{\beta}(\omega_3)f_{\beta}(\omega_4) \\ &\quad \left. + (c_{||} - c_{\perp})P_{34}f_{\alpha_1}(\omega_3)f_{\alpha_2}(\omega_4)\right\} \\ &\quad \times \delta(\omega_1 + \dots + \omega_4)d\omega_3d\omega_4, \end{aligned} \quad (6.2.38)$$

where

$$f_{\alpha}(\omega) = (2\pi)^{-1/2} \int \exp(i\omega t)f_{\alpha}(t)dt. \quad (6.2.39)$$

Expression (6.2.38) must be added to the correlator $\langle v_{\alpha_1}(\omega_1), v_{\alpha_2}(\omega_2) \rangle_0$ of a linear approximation in order to find the nonequilibrium correlator $\langle v_{\alpha_1}(\omega_1), v_{\alpha_2}(\omega_2) \rangle_f$ describing the action of an external force $f(t)$.

Similarly, by using (6.1.126) we can find the nonequilibrium correlator $\langle v_1, v_2, v_3 \rangle_f = \tilde{Y}_{123,4}f_4$ due to the action of an external force. We shall confine ourselves to finding, from (6.1.118), the fourfold correlator in the region $t_1 > t_2 > t_3 > t_4$. The matrix $d_{\alpha\beta}$ being delta-shaped, (6.1.120a) has a trivial solution:

$$m_{\alpha\beta\gamma\delta} = -\frac{m}{2\gamma}f_{\alpha\beta\gamma\delta}. \quad (6.2.40)$$

The left-hand side of (6.1.120b) vanishes, thus indicating that the integrand in the appropriate integral in (6.1.117) is independent of t_0 and that the integral is trivial.

Taking the integral gives

$$\begin{aligned} & \langle v_{\alpha_1}(t_1), \dots, v_{\alpha_4}(t_4) \rangle \\ &= \left(\frac{kT}{m} \right)^3 \left\{ \frac{\lambda}{\gamma} (P_{(234)} \delta_{\alpha_1 \alpha_2} \delta_{\alpha_3 \alpha_4}) \{ \exp[-(\gamma/m)(t_{12} + t_{13} + t_{14})] \right. \\ & \quad - 2 \exp[-(\gamma/m)(t_{12} + t_{24})] + \exp[-(\gamma/m)(t_{14} + t_{24} + t_{34})] \} \\ & \quad \left. + m^{-1} q_{\alpha_1 \alpha_2 \alpha_3 \alpha_4} t_{23} \exp[-(\gamma/m)(t_{13} + t_{24})] \right\} \end{aligned} \quad (6.2.41)$$

for $t_1 > t_2 > t_3 > t_4$. In other regions of ordered times the correlator has the same form, the only departure being the order of subscripts 1, 2, 3 and 4.

6.2.5 A Circuit with Inductance in the Non-Markov Case

Let us now return to the circuit shown in Fig. 6.1 (Sects. 4.5.2 and 6.2.1), but we will now assume the inductance to be linear and instead of (4.5.14) we will take the symmetric cubic current–voltage characteristic of a nonlinear resistance:

$$V(I) = RI + \frac{1}{6}\lambda I^3. \quad (6.2.42)$$

We will also insert in series some linear two-terminal impedor having the impedance $z(i\omega)$ (Fig. 6.2). The balance of voltages will then be given by

$$[i\omega L + R + z(i\omega)]I + \lambda I^3/6 = \tilde{h} \quad (6.2.43)$$

or

$$\dot{p} - \tilde{h} = -RI - z(d/dt)I - \frac{1}{6}\lambda I^3. \quad (6.2.44)$$

If we put here $z(i\omega) = 0$, then, comparing with (6.1.81) at $A_1 = I$, we easily find $r_{11}^{-1}d_{11} = R$, $r_{11}^{-1}f_{1111} = -\lambda$ or

$$d_{11} = R/L, \quad (6.2.45)$$

$$f_{1111} = -\lambda/L,$$

since $r_{11} = 1/L$.

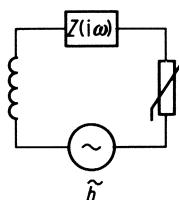


Fig. 6.2. The previous circuit now including a linear two-terminal impedor connected in series

Since the impedance $z(i\omega)$ of the two-terminal impedor may be arbitrary, the system at hand becomes non-Markovian. The presence of the two-terminal impedor $z(i\omega)$ changes the linear impedance of the system, which now becomes

$$\tilde{Z}_{1,1}(\omega_1, \omega_2) = [i\omega_2 L + R + z(i\omega_2)] \delta(\omega_1 + \omega_2), \quad (6.2.46)$$

i.e.

$$\tilde{Z}'(\omega) = i\omega L + R + z(i\omega),$$

if we make allowances for the impedance $\tilde{Z}_{1,1}(\omega_1, \omega_2)$ being contravariant.

The addition of the two-terminal impedor, however, leaves the cubic impedance and the function $\tilde{Z}_{11,11}$ unchanged. The latter has the same form as in the Markov case, where there is no two-terminal impedor $z(i\omega)$, i.e. where (6.1.107) is valid for the dissipationally undeterminable function (6.1.109). To obtain the dissipationally undeterminable function $Y_{11,11}^{(2)}$ it is sufficient to apply (6.1.90) for a new linear admittance function $Y_{1,1}$. It is obtained by finding the inverse of the matrix (6.2.46):

$$\tilde{Y}_{1,1}(\omega_1, \omega_2) = [i\omega_1 L + R + z(i\omega_1)]^{-1} \delta(\omega_1 + \omega_2). \quad (6.2.47)$$

Therefore, in (6.1.111) we should substitute $Y'(\omega_1) = [i\omega_1 L + R + z(i\omega_1)]^{-1}$ for $(i\omega_1 + \hat{D}_1)^{-1} \hat{R}_1$. Consequently, passing to the non-Markov case does not increase the number of dissipationally undeterminable parameters.

To obtain the cubic admittance in (6.1.86) we should also use the admittance (6.2.47) instead of the earlier Markov admittance (6.1.68). This same change also needs to be effected in other relationships.

We have $s_{1111} = 0$ because the inductance is linear. Using this and also (6.2.45) and substituting, as indicated above, $[i\omega_1 L + R + z(i\omega_1)]^{-1}$ for $(i\omega_1 + d_{11})^{-1} r_{11}$, from (6.1.113) we will have

$$\begin{aligned} \langle I_1(\omega_1), \dots, I_4(\omega_4) \rangle &= (kT)^3 (2\pi)^{-1} \{ - (2\lambda/L) P_{(1234)} \operatorname{Re}[i\omega_1 L \\ &\quad + R + z(i\omega_1)]^{-1} [-i\omega_2 L \\ &\quad + R + z(-i\omega_2)]^{-1} [-i\omega_3 L \\ &\quad + R + z(-i\omega_3)]^{-1} \\ &\quad \times [-i\omega_4 + R + z(-i\omega_4)]^{-1} \\ &\quad + q_{1111} P_{14}(P_{(234)} [i\omega_1 L + R \\ &\quad + z(i\omega_1)]^{-1} [i\omega_2 L + R + z(i\omega_2)]^{-1} \\ &\quad \times [-i\omega_3 L + R + z(-i\omega_3)]^{-1} \\ &\quad \times [-i\omega_4 L + R + z(-i\omega_4)]^{-1} \} \\ &\quad \times \delta(\omega_1 + \omega_2 + \omega_3 + \omega_4). \end{aligned} \quad (6.2.48)$$

The expression in front of the delta function in (6.2.48) at $\omega_4 = -\omega_1 - \omega_2 - \omega_3$ constitutes, by the definition given in Appendix A6 [equation (A6.2)], the spectral density $S(\omega_1, \omega_2, \omega_3)$ of the current.

Similarly, using (6.1.122) gives

$$\begin{aligned}
 & \delta^2 \langle I(\omega_1), I(\omega_2) \rangle / \delta \tilde{h}(\omega_3) \delta \tilde{h}(\omega_4) \\
 &= kT(2\pi)^{-1} \{ -(\lambda/L) P_{12} [(\mathrm{i}\omega_1 L + z(\mathrm{i}\omega_1) + R)^{-1} \\
 &\quad \times (-\mathrm{i}\omega_2 L + z(-\mathrm{i}\omega_2) + R)^{-1} (-\mathrm{i}\omega_3 L + z(-\mathrm{i}\omega_3) + R)^{-1} \\
 &\quad \times (-\mathrm{i}\omega_4 L + z(-\mathrm{i}\omega_4) + R)^{-1}] + q_{1111} (\mathrm{i}\omega_1 L + z(\mathrm{i}\omega_1) + R)^{-1} \\
 &\quad \times (\mathrm{i}\omega_2 L + z(\mathrm{i}\omega_2) + R)^{-1} (-\mathrm{i}\omega_3 L + z(-\mathrm{i}\omega_3) + R)^{-1} \\
 &\quad \times (-\mathrm{i}\omega_4 L + z(-\mathrm{i}\omega_4) + R)^{-1} \\
 &\quad \times \delta(\omega_1 + \omega_2 + \omega_3 + \omega_4),
 \end{aligned} \tag{6.2.49}$$

and using (6.1.126), with the above substitution, gives

$$\begin{aligned}
 & \delta^3 \langle I(\omega_1), I(\omega_2), I(\omega_3) \rangle / \delta \tilde{h}(\omega_4) \\
 &= (kT)^2 (2\pi)^{-1} \{ -(\lambda/L) P_{(123)} [(\mathrm{i}\omega_1 L + z(\mathrm{i}\omega_1) + R)^{-1} \\
 &\quad \times (-\mathrm{i}\omega_2 L + z(-\mathrm{i}\omega_2) + R)^{-1} (-\mathrm{i}\omega_3 L + z(-\mathrm{i}\omega_3) + R)^{-1} \\
 &\quad \times (-\mathrm{i}\omega_4 L + z(-\mathrm{i}\omega_4) + R)^{-1}] \\
 &\quad - (\lambda/L) (\mathrm{i}\omega_1 L + z(\mathrm{i}\omega_1) + R)^{-1} (\mathrm{i}\omega_2 L + z(\mathrm{i}\omega_2) + R)^{-1} \\
 &\quad \times (\mathrm{i}\omega_3 L + z(\mathrm{i}\omega_3) + R)^{-1} (-\mathrm{i}\omega_4 L + z(-\mathrm{i}\omega_4) + R)^{-1} \\
 &\quad + q_{1111} P_{(123)} (\mathrm{i}\omega_1 L + z(\mathrm{i}\omega_1) + R)^{-1} \\
 &\quad \times (\mathrm{i}\omega_2 L + z(\mathrm{i}\omega_2) + R)^{-1} (-\mathrm{i}\omega_3 L + z(-\mathrm{i}\omega_3) + R)^{-1} \\
 &\quad \times (-\mathrm{i}\omega_4 L + z(-\mathrm{i}\omega_4) + R)^{-1} \\
 &\quad \times \delta(\omega_1 + \omega_2 + \omega_3 + \omega_4).
 \end{aligned} \tag{6.2.50}$$

Thus, despite the fact that $z(\mathrm{i}\omega)$ may be given by a fairly complex expression, we have here only one dissipationally undeterminable parameter q_{1111} .

By way of example we will look at two specific forms of the impedance $z(\mathrm{i}\omega)$. If $z(\mathrm{i}\omega) = z_0 \exp(-\mathrm{i}\omega\tau)$, then the inserted two-terminal impedor will give a time delay τ . In this case, the system at hand is non-Markovian. The second special case occurs if we put $z(\mathrm{i}\omega) = (\mathrm{i}\omega C)^{-1}$. This means that the two-terminal impedor is a capacitance. The circuit of Fig. 6.2 will then coincide with that of Fig. 4.6, just as in the example in Sect. 4.5.6. In that case, we have a two-component Markov system. The use of (6.2.48–50) here enables us to avoid dealing with matrices and matrix relations.

6.2.6 Threefold Spectral Density of the Concentration of Diffusing Gas

The examples we have dealt with so far in this section are systems with lumped parameters. We will now turn to systems with distributed parameters. Our first example will be linearly diffusing gas. Its molar density $c(\mathbf{r}, t)$ obeys the conven-

tional equation of diffusion,

$$\dot{c}(\mathbf{r}) = D \Delta c(\mathbf{r}), \quad (6.2.51)$$

where Δ is the Laplacian and D is the diffusion coefficient.

In a first (linear) approximation the gas density fluctuations may be thought of as Gaussian. In a higher approximation they are non-Gaussian because the free energy varies with $c(\mathbf{r})$ in a nonquadratic manner. In Sect. 3.4.6 we have determined the exact kinetic potential of the diffusing gas in the ideal gas model. Consequently, we know the total master equation from which we can work out various correlators within any accuracy. By applying the theory of Sect. 6.1 we will derive here the threefold correlator in its spectral form, or rather the corresponding spectral density.

In this example we take A_α to be $c(\mathbf{r}) - c_0$, i.e. the subscript α is continuous in nature and coincides with the position vector. Comparing (6.2.51) with (6.2.25), which is equivalent to (6.1.1), we obtain the matrices $d_{\alpha\beta}$ and $f_{\alpha\beta\gamma}$, i.e. the matrices $d(\mathbf{r}, \mathbf{r}')$ and $f(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ corresponding to the given case

$$\begin{aligned} d(\mathbf{r}, \mathbf{r}') &= -\Delta_r \delta(\mathbf{r} - \mathbf{r}'), \\ f(\mathbf{r}, \mathbf{r}', \mathbf{r}'') &= 0 \end{aligned} \quad (6.2.52)$$

for $D = 1$. Furthermore, comparing (3.4.74) with (6.1.2) gives

$$\begin{aligned} (\hat{R})_{rr'} &= \frac{c_0}{RT} \delta(\mathbf{r} - \mathbf{r}'), \\ s(\mathbf{r}, \mathbf{r}', \mathbf{r}'') &= -RTc_0^{-2} \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}''). \end{aligned} \quad (6.2.53)$$

Knowing (6.2.52, 53), we can now compute the threefold correlator from (6.1.41):

$$\begin{aligned} \langle c(\mathbf{r}_1, \omega_1), c(\mathbf{r}_2, \omega_2), c(\mathbf{r}_3, \omega_3) \rangle &= (2\pi)^{-1/2} c_0 N_A^{-2} P_{123} \\ &\times [(\mathrm{i}\omega_1 - \Delta)_1^{-1} \delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &\times (-\mathrm{i}\omega_3 - \Delta)_3^{-1}] \delta(\omega_1 + \omega_2 + \omega_3). \end{aligned} \quad (6.2.54)$$

The right-hand side of this relationship includes Laplacians. To get rid of them, instead of writing the operator as $(\mathrm{i}\omega_1 - \Delta)^{-1}$ we can either carry out integration with an appropriate Green's function, or simply use the spectral representation

$$\begin{aligned} c(\mathbf{k}, \omega) &= (2\pi)^{-3/2} \int \exp(\mathrm{i}\mathbf{k}\mathbf{r}) c(\mathbf{r}, \omega) d\mathbf{r} \\ &= (2\pi)^{-2} \int \exp(\mathrm{i}\mathbf{k}\mathbf{r} - \mathrm{i}\omega t) c(\mathbf{r}, t) d\mathbf{r} dt. \end{aligned} \quad (6.2.55)$$

In so doing, from (6.2.54) we get

$$\begin{aligned} \langle c(\mathbf{k}_1, \omega_1), c(\mathbf{k}_2, \omega_2), c(\mathbf{k}_3, \omega_3) \rangle \\ = S(\mathbf{k}_1, \omega_1, \mathbf{k}_2, \omega_2) \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \delta(\omega_1 + \omega_2 + \omega_3), \end{aligned} \quad (6.2.56)$$

where S , by the definition given in Appendix 6, is the combined spectral density, which here is given by

$$S(\mathbf{k}_1, \omega_1, \mathbf{k}_2, \omega_2) = (2\pi)^{-2} c_0 N_A^{-2} P_{123} [(\mathrm{i}\omega_1 + k_1^2)^{-2} (-\mathrm{i}\omega_3 + k_3^2)^{-1}], \quad (6.2.57)$$

where $\omega_3 = -\omega_1 - \omega_2$. In addition, we can also write the equations

$$\begin{aligned} \langle c(\mathbf{k}_1, \omega_1), c(\mathbf{k}_2, \omega_2) \rangle &= S(\mathbf{k}_1, \omega_1) \delta(\mathbf{k}_1 + \mathbf{k}_2) \delta(\omega_1 + \omega_2) \\ S(\mathbf{k}_1, \omega_1) &= 2c_0 N_A^{-1} k_1^2 (\omega_1^2 + k_1^4)^{-1}, \end{aligned} \quad (6.2.58)$$

which can be conveniently derived from the linear FDR (6.1.25) and also from (6.1.5).

6.2.7 Impedances and Admittances of an Electromagnetic Field in a Cubically Nonlinear Medium

The case of cubic nonlinearity in the dependences $\mathbf{D}(E)$ and $\mathbf{j}(E)$ has been treated in Sect. 4.5.8, where the medium was assumed to be isotropic. In that case

$$D_k = \varepsilon_1 E_k + \varepsilon_3 E^2 E_k, \quad (6.2.59a)$$

$$j_k = \sigma E_k + \lambda E^2 E_k. \quad (6.2.59b)$$

We will now take a closer look at the situation. From (6.2.59a) we can easily derive

$$E_k = \varepsilon_1^{-1} (D_k - \varepsilon_1^{-3} \varepsilon_3 D^2 D_k) + O(D^4). \quad (6.2.60)$$

Here, from (4.4.90) we have $E_k = \partial u / \partial D_k$. Integrating

$$\partial u / \partial D_k = \varepsilon_1^{-1} D_k - \varepsilon_1^{-4} \varepsilon_3 D^2 D_k \quad (6.2.61)$$

gives

$$u(\mathbf{D}, \mathbf{B}) = \frac{1}{2} \varepsilon_1^{-1} D^2 - \frac{1}{4} \varepsilon_1^{-4} \varepsilon_3 D^4 + \text{const}(\mathbf{B}) \quad (6.2.62)$$

or, if we take (4.4.89) into account,

$$u(\mathbf{D}, \mathbf{B}) = \frac{1}{2} (\varepsilon_1^{-1} D^2 + \mu^{-1} B^2) - \frac{1}{4} \varepsilon_1^{-4} \varepsilon_3 D^4 + \text{const}. \quad (6.2.63)$$

Knowing the energy density (6.2.63), and hence the total energy (4.4.88) and the phenomenological equation (4.5.99), we can take the variables $\mathbf{D}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ as an internal parameter vector \mathbf{A} to determine, via the formulas of Sects. 6.1.4–7, the fourfold correlator (to dissipationally undeterminable parameters) and the four-subscript derivatives of the correlators with respect to the forces. To this end, we will of course have to invert the 6×6 -matrix $Z_{\alpha, \beta}(\omega_1, \omega_2)$ to find $Y_{\alpha, \beta}(\omega_1, \omega_2)$. To simplify our reasoning we will follow another path. Let our vector of the internal parameters, \mathbf{A} , be $\mathbf{E}(\mathbf{r})$. The role of the parameters $\tilde{\mathbf{A}}$ [see (6.1.60)] will then be played by variables having the property $d\tilde{\mathbf{A}}/dt = \mathbf{E}(\mathbf{r})$. It is easily seen that there is a simple relationship between $\tilde{\mathbf{A}}$ and the vector potential $\mathbf{A}(\mathbf{r})$, taken in the gauge in which the equalities

$$\mathbf{E}(\mathbf{r}) = -\dot{\mathbf{A}}(\mathbf{r}), \quad (6.2.64)$$

$$\mathbf{B}(\mathbf{r}) = \text{curl } \mathbf{A}(\mathbf{r}),$$

are valid. Clearly, $\tilde{\mathbf{A}}$ coincides with $-\mathbf{A}(\mathbf{r})$.

If there are external (in relation to the field) charges and currents, then it is known that they are associated with the additional energy

$$V = \int (\varphi \rho^{\text{ext}} - \mathbf{A} \cdot \mathbf{j}^{\text{ext}}) d\mathbf{r}. \quad (6.2.65)$$

For the gauge (6.2.64) the scalar potential is zero, and (6.2.65) takes the form

$$V = - \int \mathbf{A}(\mathbf{r}) \cdot \mathbf{j}^{\text{ext}}(\mathbf{r}) d\mathbf{r}. \quad (6.2.66)$$

This expression should be compared with the expression $V = - \tilde{A}_\alpha \tilde{h}_\alpha$, which defines the additional energy due to the action of the external forces $\tilde{\mathbf{h}}$ conjugate to $\tilde{\mathbf{A}}$. Since $\tilde{\mathbf{A}} = - \mathbf{A}(\mathbf{r})$, we have

$$\tilde{\mathbf{h}} = - \mathbf{j}^{\text{ext}}(\mathbf{r}). \quad (6.2.67)$$

In the presence of external currents, we will have, instead of (6.2.59b),

$$j_k = \sigma E_k + \lambda E^2 E_k + j_k^{\text{ext}}. \quad (6.2.68)$$

Substituting (6.2.59a) and also (6.2.64, 68) into Maxwell's equations (4.4.92) gives

$$\left(\varepsilon_1 \frac{\partial}{\partial t} + \sigma \right) \dot{\mathbf{A}} + \mu^{-1} (\text{grad div } \mathbf{A} - \Delta \mathbf{A}) + \left(\varepsilon_3 \frac{\partial}{\partial t} + \lambda \right) |\dot{\mathbf{A}}|^2 \dot{\mathbf{A}} = \mathbf{j}^{\text{ext}}. \quad (6.2.69)$$

By virtue of the equations $\mathbf{E} = \tilde{\mathbf{J}} = - \dot{\mathbf{A}}(\mathbf{r})$ and $\mathbf{j}^{\text{ext}} = - \tilde{\mathbf{h}}$, this equation is a special case of (6.1.82) for the case under consideration. By introducing the operator $p = \partial/\partial t$ we can write (6.2.69) as follows:

$$(p\varepsilon_1 + \sigma) \tilde{\mathbf{J}} - (p\mu)^{-1} [\nabla^2 \tilde{\mathbf{J}} - \nabla(\nabla \cdot \tilde{\mathbf{J}})] + (p\varepsilon_3 + \lambda) |\tilde{\mathbf{J}}|^2 \tilde{\mathbf{J}} = \tilde{\mathbf{h}}. \quad (6.2.70)$$

Comparison of this with the conventional equations

$$\tilde{Z}_{1,2} J_2 + \frac{1}{6} \tilde{Z}_{1,234} \tilde{J}_2 \tilde{J}_3 \tilde{J}_4 = \tilde{h}_1 \quad (6.2.71)$$

gives the linear and cubic impedances

$$\begin{aligned} \tilde{Z}_{1,2} &= (p_1 \mu)^{-1} \{ [p_1 \mu(p_1 \varepsilon_1 + \sigma) - \nabla_1^2] \delta_{j_1 j_2} + \nabla_{j_1} \nabla_{j_2} \} \delta(\mathbf{r}_{12}) \delta(t_{12}), \\ \tilde{Z}_{1,234} &= 2(p_1 \varepsilon_3 + \lambda) I_{j_1 j_2 j_3 j_4} \delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \delta(t_1, t_2, t_3, t_4), \end{aligned} \quad (6.2.72)$$

where

$$I_{jlmn} = \delta_{jl} \delta_{mn} + \delta_{jm} \delta_{ln} + \delta_{jn} \delta_{lm}.$$

In the spectral representation, (6.2.72) assumes the form

$$\begin{aligned} \tilde{Z}_{j,l}(\mathbf{k}, \omega, \mathbf{k}', \omega') \\ = (-i\omega\mu)^{-1} \{ [i\omega\mu(i\omega\varepsilon_1 - \sigma) + k^2] \delta_{jl} - k_j k_l \} \delta(\mathbf{k} + \mathbf{k}') \delta(\omega + \omega'), \end{aligned} \quad (6.2.73)$$

$$\tilde{Z}_{1,234} = 2(2\pi)^{-4} (-i\omega_1 \varepsilon_3 + \lambda) I_{j_1 j_2 j_3 j_4} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4) \delta(\omega_1 + \dots + \omega_4). \quad (6.2.74)$$

Here we have substituted $-i\omega$ for p , because, unlike admittances, impedances are

contravariant in the sense of Sect. 5.2.2. The expression $i\omega\varepsilon_1 + \sigma$ will be treated as $i\omega(\omega)$, where $\varepsilon(\omega)$ is the total linear permittivity.

Inverting the linear impedance (6.2.73) by the relation $Y_{12} = Z_{12}^{-1}$ we find the appropriate admittance

$$\begin{aligned}\tilde{Y}_{j,l}(\mathbf{k}, \omega, \mathbf{k}', \omega') &= i\omega\mu[k^2 - \omega^2\mu\varepsilon(\omega)]^{-1} \left[\delta_{jl} - \frac{k_j k_l}{\omega^2\mu\varepsilon(\omega)} \right] \delta(\mathbf{k} + \mathbf{k}') \delta(\omega + \omega') \\ &\equiv y_{jl}(\mathbf{k}, \omega) \delta(\mathbf{k} + \mathbf{k}') \delta(\omega + \omega').\end{aligned}\quad (6.2.75)$$

This expression can be verified directly by computing the matrix product $Z_{1,2} Y_{2,3}$. Applying now the formula $\beta \langle I_1, I_2 \rangle_0 = Y_{1,2} + Y_{2,1}$ corresponding to (5.3.92), we can easily find the twofold correlator

$$\begin{aligned}\beta \langle E_j(\mathbf{k}, \omega), E_l(\mathbf{k}', \omega') \rangle_0 &= -\omega\mu \text{Im} \left\{ [k^2 - \omega^2\mu\varepsilon(\omega)]^{-1} \left[\delta_{jl} - \frac{k_j k_l}{\omega^2\mu\varepsilon(\omega)} \right] \right\} \delta(\mathbf{k} + \mathbf{k}') \delta(\omega + \omega').\end{aligned}\quad (6.2.76)$$

The subscript 0 on the left signifies that the correlator is for zero external currents j^{ext} .

6.2.8 Dissipationally Undeterminable Functions and the Fourfold Correlator of an Electromagnetic Field

We now wish to find the fourfold correlator of an electric field in the spectral representation. Knowing the cubic impedance (6.2.74) and the linear admittance (6.2.75), we can write the cubic admittance as

$$\begin{aligned}\tilde{Y}_{1,234} &= -\tilde{Y}_1 \tilde{Z}_{1,234} \tilde{Y}_2 \tilde{Y}_3 \tilde{Y}_4 \\ &= -2(2\pi)^{-4}(i\omega_1\varepsilon_3 + \lambda)y_{j_1l}(\mathbf{k}_1, \omega_1)I_{lmns}y_{mj_2}^*(\mathbf{k}_2, \omega_2)y_{nj_3}^*(\mathbf{k}_3, \omega_3) \\ &\quad \times y_{sj_4}^*(\mathbf{k}_4, \omega_4)\delta(\mathbf{k}_1 + \dots + \mathbf{k}_4)\delta(\omega_1 + \dots + \omega_4).\end{aligned}\quad (6.2.77)$$

It enables us to find the dissipationally determinable parts (5.4.109) of four-subscript functions, in particular the fourfold correlator. We will now compute their dissipationally undeterminable parts by the same technique as in Sects. 6.1.5, 6. In Sect. 4.5.8 we found the coefficients (4.5.103) of the master equation, which correspond to the phenomenological equations (4.5.99). If we introduce into these equations the fluctuations described by the above-mentioned coefficients, we will have the following Langevin equation:

$$\dot{D}_l = (\text{curl } \mathbf{H})_l - \mathbf{j}_l(\mathbf{E}) + \eta_l(\mathbf{r}, t, \mathbf{E}) \quad (6.2.78)$$

(the second equation is of no interest to us). Here $\eta_l(\mathbf{r}, t) = -(\mathbf{j}_f)_l$ are fluctuation effects which have the physical meaning of external currents taken with the opposite sign. Their statistical properties are governed by the coefficients of the

master equation

$$\langle \eta_{l_1}(\mathbf{r}_1, t_1), \dots, \eta_{l_m}(\mathbf{r}_m, t_m) \rangle_E = K_{l_1 \dots l_m}(\mathbf{r}_1, \dots, \mathbf{r}_m, E) \delta(t_1, \dots, t_m), \quad (6.2.79)$$

where on the left we have conditional correlators that correspond to the fixed vector E . Using (4.5.103c), we thus have

$$\begin{aligned} & \langle \eta_j(\mathbf{r}_1, t_1), \eta_l(\mathbf{r}_2, t_2) \rangle_E \\ &= kT[2\sigma\delta_{jl} + (2\lambda + c_1 + c_2)E^2\delta_{jl} + (4\lambda + 2c_2)E_jE_l]\delta(\mathbf{r}_{12})\delta(t_{12}). \end{aligned} \quad (6.2.80)$$

On the other hand, in this case, as in others, the stochastic representation (5.7.58) is valid; here however we have to substitute \tilde{J} for J . By (5.6.99b) we will have

$$\langle \tilde{\mathcal{E}}_1, \tilde{\mathcal{E}}_2 \rangle_{\tilde{J}} = \tilde{Z}_{12} + \frac{1}{2}\tilde{Z}_{12,34}\tilde{J}_3\tilde{J}_4. \quad (6.2.81)$$

As mentioned earlier, $\tilde{J} = E(r)$. What physical meaning can be attached to the random forces $\tilde{\mathcal{E}}$? Generally speaking, the stochastic equation

$$\tilde{Z}_{1,2}J_2 + \frac{1}{6}\tilde{Z}_{1,234}\tilde{J}_2\tilde{J}_3\tilde{J}_4 = \tilde{h}_1 + \tilde{\mathcal{E}}_1 \quad (6.2.82)$$

of the type (5.7.4) holds. This now plays the part of (6.2.71). However, in our case $\tilde{h}_1 = -j^{\text{ext}}(r)$. Therefore, $\tilde{h}_1 + \tilde{\mathcal{E}}_1$ clearly has the sense of $-j^{\text{ext}} - j_f$, i.e. $\tilde{\mathcal{E}}_1 = -j_f(r)$. Recalling that $\eta(r) = -j_f(r)$ we see that $\tilde{\mathcal{E}}$ coincides with $\eta(r)$. Therefore, (6.2.80) coincides with (6.2.81) and from (6.2.80) we can easily find $Z_{12,34}$. Differentiating the right-hand side of (6.2.80) with respect to E_{j_3} and E_{j_4} gives

$$\begin{aligned} \tilde{Z}_{12,34} &= kT[2(2\lambda + c_1 + c_2)\delta_{j_1j_2}\delta_{j_3j_4} + (4\lambda + 2c_2)(\delta_{j_1j_3}\delta_{j_2j_4} + \delta_{j_1j_4}\delta_{j_2j_3})] \\ &\times \delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)\delta(t_1, t_2, t_3, t_4). \end{aligned} \quad (6.2.83)$$

Using (6.2.83) and the cubic impedance from (6.2.72) we can, according to (6.1.107), now obtain the dissipationally undeterminable function

$$\begin{aligned} \beta\tilde{Z}_{12,34}^{(2)} &= 2\{c_1\delta_{j_1j_2}\delta_{j_3j_4} + [c_2 - (p_1 + p_2)\varepsilon_3]I_{j_1j_2j_3j_4}\} \\ &\times \delta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)\delta(t_1, t_2, t_3, t_4), \end{aligned} \quad (6.2.84)$$

or in the spectral representation

$$\begin{aligned} \beta\tilde{Z}_{12,34}^{(2)} &= (2\pi)^{-4}\{2c_1\delta_{j_1j_2}\delta_{j_3j_4} + [2c_2 + 2i(\omega_1 + \omega_2)]I_{j_1\dots j_4}\} \\ &\times \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4)\delta(\omega_1 + \dots + \omega_4). \end{aligned} \quad (6.2.85)$$

From (6.1.90), using (6.2.75), we can now find the appropriate $Y^{(2)}$:

$$\begin{aligned} \beta\tilde{Y}_{12,34}^{(2)} &= 2(2\pi)^{-4}y_{j_1l}(\mathbf{k}_1, \omega_1)y_{j_2m}(\mathbf{k}_2, \omega_2) \\ &\times [c_1\delta_{lm}\delta_{ns} + (c_2 - i\omega_1 - i\omega_2)I_{lmns}]y_{nj_3}^*(\mathbf{k}_3, \omega_3)y_{sj_4}^*(\mathbf{k}_4, \omega_4) \\ &\times \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4)\delta(\omega_1 + \dots + \omega_4). \end{aligned} \quad (6.2.86)$$

The equalities (6.2.77) and (6.2.86) enable us to find the correlator for the electric field. To this end, we will have to use the FDR

$$\beta^3 Y_{1234} = P_{(1234)}(Y_{1,234} + Y_{1,234}^{\text{rc}}) + \beta P_{(234)}[P_{14} Y_{12,34}^{(2)}] \quad (6.2.87)$$

of Sect. 5.4.9. We thus arrive at

$$\begin{aligned} \beta^3 \langle E_1, E_2, E_3, E_4 \rangle &= 2(2\pi)^{-4} \{ -P_{(1234)}[2 \operatorname{Re}(i\omega_1 \varepsilon_3 + \lambda) \\ &\times y_{j_1 l}(\mathbf{k}_1, \omega_1) I_{lmns} y_{mj_2}^*(\mathbf{k}_2, \omega_2) y_{nj_3}^*(\mathbf{k}_3, \omega_3) y_{sj_4}^*(\mathbf{k}_4, \omega_4)] \\ &+ P_{(234)}[P_{14} y_{j_1 l}(\mathbf{k}_1, \omega_1) y_{j_2 m}(\mathbf{k}_2, \omega_2) \\ &(c_1 \delta_{lm} \delta_{ns} + (c_2 - i\omega_1 - i\omega_2) I_{lmns}) y_{nj_3}^*(\mathbf{k}_3, \omega_3) y_{sj_4}^*(\mathbf{k}_4, \omega_4)] \} \\ &\times \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4) \delta(\omega_1 + \dots + \omega_4), \end{aligned} \quad (6.2.88)$$

which is the desired fourfold space-time spectral density of fluctuations of the field \mathbf{E} .

Furthermore, from the equations

$$\begin{aligned} \beta^2 \tilde{Y}_{123,4} &= P_{(123)} \tilde{Y}_{1,234} + \tilde{Y}_{4,123}^{t,c} + \beta P_{(123)} \tilde{Y}_{12,34}^{(2)}, \\ \beta \tilde{Y}_{12,34} &= P_{12} \tilde{Y}_{1,234} + \beta \tilde{Y}_{12,34}^{(2)}, \end{aligned} \quad (6.2.89)$$

i.e. the FDRs of Sect. 5.4.9, we can find the derivatives

$$\begin{aligned} \delta \langle E_1, E_2, E_3 \rangle / \delta j_4^{\text{ext}} &= - \tilde{Y}_{123,4}, \\ \delta^2 \langle E_1, E_2 \rangle / \delta j_3^{\text{ext}} \cdot \delta j_4^{\text{ext}} &= \tilde{Y}_{12,34} \end{aligned} \quad (6.2.90)$$

and hence the nonequilibrium correlators

$$\begin{aligned} \langle E_1, E_2, E_3 \rangle &= - \tilde{Y}_{123,4} j_4^{\text{ext}}, \\ \langle E_1, E_2 \rangle &= \langle E_1, E_2 \rangle_0 + \frac{1}{2} \tilde{Y}_{12,34} j_3^{\text{ext}} j_4^{\text{ext}}. \end{aligned} \quad (6.2.91)$$

The functions will each contain only two dissipationally undeterminable constants c_1 and c_2 .

The results derived, as shown above, can also be generalized to the non-Markov case with spatial and/or temporal dispersion. With both dispersions, (6.2.59b) will be replaced by

$$\begin{aligned} j_k(\mathbf{r}, t) &= \int \sigma(\mathbf{r} - \mathbf{r}', t - t') E_k(\mathbf{r}', t') d\mathbf{r}' dt' \\ &+ \int \lambda(\mathbf{r} - \mathbf{r}_1, \mathbf{r} - \mathbf{r}_2, \mathbf{r} - \mathbf{r}_3, t - t_1, t - t_2, t - t_3) \\ &\times E_j(\mathbf{r}_1, t_1) E_j(\mathbf{r}_2, t_2) E_k(\mathbf{r}_3, t_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 dt_1 dt_2 dt_3 \end{aligned} \quad (6.2.92)$$

and similarly for (6.2.59a). In spectral language this means that σ and ε_1 become functions of \mathbf{k} and ω , and λ, ε_3 become functions of $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \omega_1, \omega_2, \omega_3$. The complete electric permittivity will now be

$$\varepsilon(\mathbf{k}, \omega) = \varepsilon_1(\mathbf{k}, \omega) + (i\omega)^{-1} \sigma(\mathbf{k}, \omega). \quad (6.2.93)$$

Equation (6.2.88) and other similar relationships derived using (6.2.89) now retain their meaning if we replace $\varepsilon_1, \sigma, \varepsilon_3$ and λ (and perhaps μ) by the appropriate functions of frequencies and wave vectors. The constants c_1 and c_2 also become

functions $c_1(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \omega_1, \omega_2, \omega_3)$ and $c_2(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \omega_1, \omega_2, \omega_3)$, and the dissipationally undeterminable factors increase in weight markedly. However, their relative weight still remains small.

In fact, the correlator $\langle E_1, E_2, E_3, E_4 \rangle$ contains 15 independent functions of $\mathbf{k}_1, \dots, \mathbf{k}_3, \omega_1, \dots, \omega_3$, since the symmetric tensor in four dimensions, whose subscripts run through the values 1, 2, 3, has 15 independent elements. The matrix $\delta \langle E_1, E_2, E_3 \rangle / \delta h_4$ can be shown to contain 30 independent functions. The matrix $\delta^2 \langle E_1, E_2 \rangle / \delta \tilde{h}_3 \delta \tilde{h}_4$ contains 36 independent functions. Altogether, there are 81 functions of $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \omega_1, \omega_2, \omega_3$ and all of them are determined by two dissipationally undeterminable functions of the same arguments.

The number of functions found, i.e. expressed in terms of c_1 and c_2 , will be still greater if we use the relation $\mathbf{B} = -(\mathrm{i}\omega)^{-1} \operatorname{curl} \mathbf{E}$, which follows from (6.2.64), to find the correlators of the magnetic field. We can remove the uncertainty that remained after the phenomenological equation was fixed by turning to one or another of the models of electrical conduction in a medium.

The correlator (6.2.88), according to

$$\langle E_1 E_2 E_3 E_4 \rangle = P_{(234)} \langle E_1, E_2 \rangle \langle E_3, E_4 \rangle + \langle E_1, E_2, E_3, E_4 \rangle, \quad (6.2.94)$$

defines the fourfold moment of the field more exactly than follows from the theory of Gaussian fluctuations, which in (6.2.94) gives rise to terms of the type $\langle E_1, E_2 \rangle \langle E_3, E_4 \rangle$. It is true that the non-Gaussian term in (6.2.94) is relatively small compared to the first terms, but it differs markedly in its behaviour. The terms $P_{(234)} \langle E_1, E_2 \rangle \langle E_3, E_4 \rangle$ are only distinct from zero on the diagonals $\mathbf{k}_1 + \mathbf{k}_2 = 0$, $\omega_1 + \omega_2 = 0$ and $\mathbf{k}_1 + \mathbf{k}_3 = 0$, $\omega_1 + \omega_3 = 0$ and $\mathbf{k}_1 + \mathbf{k}_4 = 0$, $\omega_1 + \omega_4 = 0$. Elsewhere the spectral density of the fluctuations is affected only by the non-Gaussian term. It follows that the non-Gaussian term – the fourfold correlator – is sometimes of significance, despite its smallness.

6.3 Other Uses of Nonlinear FDRs

6.3.1 Calculation of $Z_{12,34}$ in the Diode Model of Nonlinear Resistance

The diode model discussed in Sects. 3.3.2–4 is illustrated in Fig. 3.1 and described by (3.3.31). In the symmetric case, i.e. that corresponding to values $p = q = 1/2$ from (3.3.20), neglecting the small terms $\beta e^2/(8C)$ in the exponential function, we obtain the following characteristic:

$$\begin{aligned} f(V) &= 2I_1 \sinh(\beta e V/2) \\ &= 2I_1 [\beta e V/2 + \frac{1}{6}(\beta e V/2)^3 + \dots] \\ &= \beta e I_1 V + \frac{1}{24} \beta^3 e^3 I_1 V^3 + \dots \end{aligned} \quad (6.3.1)$$

Equation (6.2.42) defines the inverse relationship $f^{-1}(I) = RI + \lambda I^3/6$. Using

iterations to determine the inverse function, we readily obtain

$$\begin{aligned} R &= (\beta e I_1)^{-1}, \\ \lambda &= -\frac{1}{4} \beta^3 e^3 I_1 (\beta e I_1)^{-4} \\ &= -(4\beta e I_1^3)^{-1}. \end{aligned} \quad (6.3.2)$$

Considering the image (3.3.37), we obtain from (3.1.41) for the diode model

$$\begin{aligned} \kappa_1(U) &= -2I_1 \sinh(\frac{1}{2}\beta e U) \\ &= -\beta e I_1 U - \frac{1}{24} \beta^3 e^3 I_1 U^3, \end{aligned} \quad (6.3.3a)$$

$$\begin{aligned} \kappa_{11}(U) &= 2eI_1 \cosh(\frac{1}{2}\beta e U) \\ &= 2eI_1 + \frac{1}{4} \beta^2 e^3 I_1 U^2. \end{aligned} \quad (6.3.3b)$$

Hence,

$$\begin{aligned} l_{1,1} &= -\beta e I_1, \\ l_{1,111} &= -\frac{1}{4} \beta^3 e^3 I_1, \\ l_{11} &= 2eI_1, \\ l_{11,11} &= \frac{1}{2} \beta^2 e^3 I_1. \end{aligned} \quad (6.3.4)$$

Thus, for these values we obtain from (4.1.26)

$$c_{11,11} = \beta l_{11,11} + 2l_{1,111} = 0, \quad (6.3.5)$$

i.e. in a given Markov example for the diode model the dissipationally undeterminable parameter $c_{11,11}$ is zero.

If we now wish to find dissipationally undeterminable parameters and functions for other circuits containing a given nonlinear resistance, it would be advisable to apply the general non-Markov analytical techniques based on the use of $Z_{1,2,\dots}$ or $Q_{1,2,\dots}$.

In order that non-Markov techniques may be applied to a given case we will introduce into the circuit shown in Fig. 3.1 an external e.m.f., h . The resultant circuit diagram is given in Fig. 6.3. In this case, instead of (3.3.19) we will have the following equation:

$$I = -f(Q/C - h). \quad (6.3.6)$$

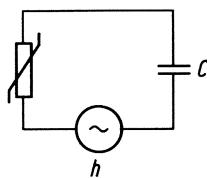


Fig. 6.3. Circuit with nonlinear resistance into which an external e.m.f. h is introduced

Solving this for $Q/C - h$ and considering, as stated above, that $f^{-1}(I) = RI + \lambda I^3/6$, we get

$$I/(pC) - h = -RI - \frac{1}{6}\lambda I^3, \quad (6.3.7)$$

i.e.

$$h = [R + (pC)^{-1}]I + \frac{1}{6}\lambda I^3. \quad (6.3.8)$$

This equation describes the voltage balance. Comparing it with (5.6.8), we obtain for this circuit the impedances

$$\begin{aligned} Z_{1,2} &= [R + (p_1 C)^{-1}] \delta(t_{12}), \\ Z_{1,234} &= \lambda \delta(t_1, t_2, t_3, t_4) \\ (Z_{1,23} &= 0). \end{aligned} \quad (6.3.9)$$

We would now like to discuss the fluctuations in the system. Since the process in the circuit of Fig. 3.1 is Markovian, for the phenomenological equation (3.3.19) we have the following Langevin equation:

$$\dot{Q} = -f(Q/C) + I_f(Q, t), \quad (6.3.10)$$

where $I_f(Q, t)$ is the delta-correlated (at fixed Q) fluctuational current:

$$\langle I_f(Q, t_1), I_f(Q, t_2) \rangle_Q = K_{11}(Q) \delta(t_{12}), \quad (6.3.11)$$

where $K_{11}(Q) = \kappa_{11}(Q/C)$ is the coefficient of the master equation. Using (6.3.3b) yields

$$\langle I_f(t_1), I_f(t_2) \rangle_Q = [2eI_1 + \frac{1}{4}\beta^2 e^3 I_1 (Q/C)^2] \delta(t_{12}). \quad (6.3.12)$$

We will now make use of the stochastic representation of the fluctuational current

$$I_f(Q, t) = \sigma(Q/C) \xi(t), \quad (6.3.13)$$

where

$$\sigma^2(U) = 2eI_1 + \frac{1}{4}\beta^2 e^3 I_1 U^2, \quad (6.3.14)$$

in order for (6.3.12) to be valid. Here $\xi(t)$ is statistically independent of Q and I . It is a random function with zero mean and the correlator

$$\langle \xi(t_1), \xi(t_2) \rangle = \delta(t_{12}). \quad (6.3.15)$$

Expression (6.3.13) should be substituted into (6.3.10).

If we include an external e.m.f. in the circuit (Fig. 6.3), then instead of (6.3.13) we will have to take the expression

$$I_f(t) = \sigma(Q/C - h) \xi(t). \quad (6.3.16)$$

Adding this to the right-hand side of the equation with force h of the type (6.3.6) gives the following Langevin equation:

$$I = -R^{-1}(Q/C - h) + \frac{1}{6}R^{-4}\lambda(Q/C - h)^3 + \sigma(Q/C - h)\xi(t). \quad (6.3.17)$$

Let us solve this for h . It is more convenient to write it as

$$I = -R^{-1}(Q/C - h - \mathcal{E}) + \frac{1}{6}R^{-4}\lambda(Q/C - h - \mathcal{E})^3 + \dots, \quad (6.3.18)$$

where \mathcal{E} is a random function given by the equation

$$R^{-1}\mathcal{E} - \frac{1}{2}R^{-4}\lambda[(Q/C - h)^2\mathcal{E} + O(\mathcal{E}^2)] = \sigma(Q/C - h)\xi(t), \quad (6.3.19)$$

which is obtained by comparing (6.3.17) and (6.3.18).

From (6.3.18) we have

$$h + \mathcal{E} - Q/C = RI + \frac{1}{6}\lambda I^3. \quad (6.3.20)$$

Hence,

$$h + \mathcal{E} = [R + (pC)^{-1}]I + \frac{1}{6}\lambda I^3. \quad (6.3.21)$$

By virtue of (6.3.9) this relationship coincides with the equation

$$h_1 + \mathcal{E}_1 = Z_{1,2}I_2 + \frac{1}{6}Z_{1,234}I_2I_3I_4, \quad (6.3.22)$$

which is equivalent to (5.7.4). Ignoring the terms $O(\mathcal{E}^2)$ in (6.3.19), we see that the fluctuational force $\mathcal{E}(t)$ has the form

$$\begin{aligned} \mathcal{E} &= [R^{-1} - \frac{1}{2}R^{-4}\lambda(Q/C - h)^2]^{-1}\sigma(Q/C - h)\xi \\ &= R[1 + \frac{1}{2}R^{-3}\lambda(Q/C - h)^2]\sigma(Q/C - h)\xi. \end{aligned} \quad (6.3.23)$$

Let us now use (6.3.14), which, as a result of (6.3.2), can be written as

$$\sigma^2(U) = kT(2R^{-1} - R^{-4}\lambda U^2). \quad (6.3.24)$$

Thus, in this approximation we have

$$\begin{aligned} \sigma(U) &= (2kTR^{-1})^{1/2}(1 - \frac{1}{2}R^{-3}\lambda U^2)^{1/2} \\ &= (2kTR^{-1})^{1/2}(1 - \frac{1}{4}R^{-3}\lambda U^2). \end{aligned} \quad (6.3.25)$$

Substitution into (6.3.23) yields

$$\mathcal{E} = (2kTR)^{1/2}[1 + \frac{1}{4}R^{-3}\lambda(Q/C - h)^2]\xi. \quad (6.3.26)$$

The terms of the order $(Q/C - h)^4$ and higher are neglected here. In (6.3.26) we can easily express $Q/C - h$ in terms of the current I by using the linear part of (6.3.17):

$$\mathcal{E} = (2kTR)^{1/2}(1 + \frac{1}{4}R^{-1}\lambda I^2)\xi. \quad (6.3.27)$$

Using this formula and (6.3.15), we will find the correlator for the fluctuational force at fixed current:

$$\begin{aligned} \langle \mathcal{E}(t_1), \mathcal{E}(t_2) \rangle_I &= 2kTR(1 + \frac{1}{2}R^{-1}\lambda I^2)\delta(t_{12}) \\ &= (2kTR + kT\lambda I^2)\delta(t_{12}). \end{aligned} \quad (6.3.28)$$

However, according to (5.6.109b) the correlator (6.3.28) must be $Z_{12} + Z_{12,34}I_3 \times I_4/2$. Comparison gives

$$Z_{12,34} = 2kT\lambda\delta(t_1, t_2, t_3, t_4). \quad (6.3.29)$$

On the other hand, according to the general theory in the nonquantum case [see (5.7.55b)] we have the relation

$$Z_{12,34} = kT(Z_{1,234} + Z_{2,134}) + Z_{12,34}^{(2)}, \quad (6.3.30)$$

which, by (6.3.9), yields

$$Z_{12,34} = 2kT\lambda\delta(t_1, t_2, t_3, t_4) + Z_{12,34}^{(2)}. \quad (6.3.31)$$

Equating (6.3.29) and (6.3.31), we obtain the dissipationally undeterminable function

$$Z_{12,34}^{(2)} = 0. \quad (6.3.32)$$

Therefore, $Y_{12,34}^{(2)}$ is zero, as is $c_{11,11}$.

6.3.2 The Dissipationally Undeterminable Function $Z_{12,34}^{(2)}$ for the Example of Sect. 6.2.5

In determining $Z_{12,34}^{(2)}$ we have so far only discussed the circuits shown in Figs. 3.1 and 6.3. Just like the impedance $Z_{1,234}$, the dissipationally undeterminable function $Z_{12,34}^{(2)}$ would not change, of course, if a given nonlinear resistance were connected into another circuit with linear elements, for instance, into the circuit of Fig. 6.2. To begin with, suppose that there is no two-terminal impedor $z(i\omega)$ represented in Fig. 6.2. According to (6.2.43), the system at hand will then be described by

$$(i\omega L + R)I + \frac{1}{6}\lambda I^3 = \tilde{h}. \quad (6.3.33)$$

This means that the linear impedance here is $Z_{1,2} = (p_1L + R)\delta(t_{12})$ and the nonlinear impedance is the same as in the previous subsection. Therefore, the functions (6.3.29, 32) will be unchanged here, and so we will be able to use (6.3.27) for the random e.m.f. as before.

We can also apply the Markov technique to the circuit under consideration. If we write the energy of the inductance as $LI^2/2$ and introduce the momentum $p = LI$, from (6.3.33) at $h = 0$, we obtain the equation

$$\dot{p} = -RI - \frac{1}{6}\lambda I^3, \quad (6.3.34)$$

which is none other than the phenomenological equation in a reduced form. Using this we get

$$l_{1,1} = -R, \quad l_{1,111} = -\lambda. \quad (6.3.35)$$

Applying (4.1.28) yields

$$l_{11,11} = kT(2\lambda + c_{11,11}), \quad (6.3.36)$$

where $c_{11,11}$ is the dissipationally undeterminable parameter of the Markov theory. It need not coincide with the appropriate parameter in Sect. 6.3.1.

Introducing a random force into (6.3.34), we obtain the Langevin equation

$$\dot{p} = -RI - \frac{1}{6}\lambda I^3 + \xi(I, t). \quad (6.3.37)$$

The random force has the correlator

$$\begin{aligned} \langle \xi(I, t_1) \xi(I, t_2) \rangle_I &= K_{11}(I) \delta(t_{12}) \\ &= (l_{11} + \frac{1}{2}l_{11,11}I^2) \delta(t_{12}) \end{aligned} \quad (6.3.38)$$

or, by (6.3.35),

$$\langle \xi(t_1), \xi(t_2) \rangle_I = kT[2R + (\lambda + \frac{1}{2}c_{11,11})I^2]\delta(t_{12}). \quad (6.3.39)$$

Since $\xi(t)$ has the sense of an e.m.f., this equality coincides with (6.3.28). Comparison gives $c_{11,11} = 0$. Furthermore, (6.3.39) coincides with the equality

$$\langle \mathcal{E}_1, \mathcal{E}_2 \rangle_J = kTZ_{12} + \frac{1}{2}kT(Z_{1,234} + Z_{2,134})J_3 J_4 + \frac{1}{2}Z_{12,34}^{(2)} J_3 J_4 \quad (6.3.40)$$

from the non-Markov theory. Here we have made use of (6.3.30). Since, according to (6.3.33) $Z_{1,234} = \lambda\delta(t_1, \dots, t_4)$, from (6.3.39, 40) we obtain

$$Z_{12,34}^{(2)} = kTc_{11,11}\delta(t_1, \dots, t_4). \quad (6.3.41)$$

Since $c_{11,11}$ vanishes, this function is zero, which agrees with (6.3.32).

Thus, the diode model of nonlinear resistance used for the circuit diagram of Fig. 3.1 enables us, just like any other model, to find dissipationally undeterminable parameters and functions for other circuits that contain a nonlinear resistance. This is true of both Markov and the non-Markov forms of the theory.

The function $Z_{12,34}^{(2)}$ is also determined by (6.3.32) in the case where the circuit includes a two-terminal impedor with impedance $z(i\omega)$ (Fig. 6.2). From (6.1.110) and the equality $s_{1111} = 0$, which follows from the inductance being linear, we have $q_{1111} = c_{11,11} = 0$. Thus, we have found the parameter q_{1111} , which enters into (6.2.48–50) describing the circuit. Of course, we could instead use other precise models.

6.3.3 Serially Connected Nonlinear Subsystems at Different Temperatures

Consider now another type of problem, namely a composite system whose component parts have different temperatures. One example is the circuit depicted in Fig. 6.4, which includes a serially connected inductance and two nonlinear resistances, each of which is in thermal contact with its own heat bath of high heat capacity, so that the temperatures T_1 and T_2 of the first and second resistances can be taken to be constant. Can we calculate the correlators of the fluctuational current in the circuit despite the fact that different parts of the system have different temperatures? Strictly speaking, the answer is no. If, however, we use FDRs of the third kind and assume that the resultant random e.m.f.'s can be attributed to their

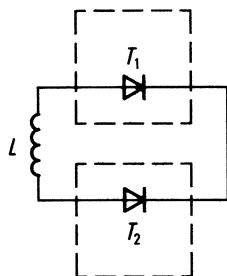


Fig. 6.4. Circuit with two nonlinear resistors at different temperatures

resistances, then this calculation is possible. The great advantage of FDRs of the third kind over FDRs of the second kind lies in the fact that with the former, fluctuational forces can be treated as being associated with their respective dissipative elements.

If two nonlinear subsystems are connected in series, then the total (or complete) impedances are the sums of the subsystem impedances

$$Z_{1,2}^c = Z_{1,2}^{(1)} + Z_{1,2}^{(2)}, \quad (6.3.42a)$$

$$Z_{1,23}^c = Z_{1,23}^{(1)} + Z_{1,23}^{(2)} \quad (6.3.42b)$$

and so on. This is because the thermodynamic forces h of the whole system are equal to the sum $h^{(1)} + h^{(2)}$, i.e. the sum of the forces due to the subsystems. Identifying the sum of the equations

$$\begin{aligned} h_1^{(2)} &= Z_{1,2}^{(2)} I_2 + \frac{1}{2} Z_{1,23}^{(2)} I_2 I_3 + \dots, \\ h_1^{(1)} &= Z_{1,2}^{(1)} I_2 + \frac{1}{2} Z_{1,23}^{(1)} I_2 I_3 + \dots \end{aligned} \quad (6.3.43)$$

with the equation

$$h_1 = Z_{1,2}^c I_2 + \frac{1}{2} Z_{1,23}^c I_2 I_3 + \dots, \quad (6.3.44)$$

we obtain (6.3.42a, b).

As an example, let us find the correlator

$$\langle I_1, I_2 \rangle = Y_{12}^c + Y_{12,3}^c h_3 \quad (6.3.45)$$

for the system.

Using (5.6.99b) for each subsystem gives

$$\langle \mathcal{E}_1^{(l)}, \mathcal{E}_2^{(l)} \rangle_I = Z_{12}^{(l)} + Z_{12,3}^{(l)} I_3, \quad l = 1, 2, \quad (6.3.46)$$

or, considering FDRs (5.6.102a, b),

$$\langle \mathcal{E}_1^{(l)}, \mathcal{E}_2^{(l)} \rangle_I = k T_l (Z_{1,2}^{(l)} + Z_{2,1}^{(l)}) + k T_l (Z_{1,23}^{(l)} + Z_{2,13}^{(l)} + Z_{3,21}^{(l,c)}) I_3. \quad (6.3.47)$$

The total random force \mathcal{E} is $\mathcal{E}^{(1)} + \mathcal{E}^{(2)}$. Since $\mathcal{E}^{(1)}$ and $\mathcal{E}^{(2)}$ are statistically independent of each other at fixed $I(\cdot)$, we have

$$\begin{aligned} \langle \mathcal{E}_1, \mathcal{E}_2 \rangle_I &\equiv Z_{12}^c + Z_{12,3}^c I_3 \\ &= \langle \mathcal{E}_1^{(1)}, \mathcal{E}_2^{(1)} \rangle + \langle \mathcal{E}_1^{(2)}, \mathcal{E}_2^{(2)} \rangle. \end{aligned} \quad (6.3.48)$$

Adding the expressions (6.3.47) for $l = 1, 2$ together yields

$$\begin{aligned} Z_{12}^c &= \sum_{l=1}^2 k T_l (Z_{1,2}^{(l)} + Z_{2,3}^{(l)}), \\ Z_{12,3}^c &= \sum_{l=1}^2 k T_l (Z_{1,23}^{(l)} + Z_{2,13}^{(l)} + Z_{3,21}^{(l,c)}). \end{aligned} \quad (6.3.49)$$

However, Z_{12}^c and $Z_{12,3}^c$ are related to Y_{12}^c and $Y_{12,3}^c$ by the conventional relationships discussed in Sects. 5.6.4–7. Thus, using the equation

$$Y_{12} = Y_1 Y_2 Z_{12}, \quad (6.3.50)$$

which is equivalent to the equation $G_{12} = G_1 G_2 Q_{12}$ which follows from (5.6.52a, 73a), we will have

$$\begin{aligned} Y_{12}^c &= Y_{1,3}^c Y_{2,4}^c Z_{34}^c \\ &= Y_{1,3}^c Y_{2,4}^c \sum_{l=1}^2 k T_l (Z_{3,4}^{(l)} + Z_{4,3}^{(l)}) . \end{aligned} \quad (6.3.51)$$

Furthermore, from (5.6.52b, 73b) we get

$$G_{12,3} = G_1 G_2 (Q_{12,3} - P_{12} Q_{1,43} Q_2 G_{24}) G_3 . \quad (6.3.52)$$

Going over to Y_{\dots} and Z_{\dots} we obtain

$$Y_{12,3}^c = Y_1^c Y_2^c (Z_{12,3}^c - Z_{1,43}^c Z_2^c Y_{24}^c - Z_{2,43}^c Z_1^c Y_{14}^c) Y_3^c \quad (6.3.53)$$

or, from (6.3.51),

$$Y_{12,3}^c = Y_1^c Y_2^c (Z_{12,3}^c - Z_{1,43}^c Y_4^c Z_{24}^c - Z_{2,43}^c Y_4^c Z_{14}^c) Y_3^c . \quad (6.3.54)$$

In (6.3.51, 53, 54) $Y_{1,2}^c = (Z_{1,2}^c)^{-1}$, the total impedances being given by (6.3.42a). Substituting (6.3.42) and (6.3.49) into (6.3.54), we obtain

$$\begin{aligned} Y_{12,3}^c &= k Y_1^c Y_2^c \sum_l \left[T_l (Z_{1,23}^{(l)} + Z_{2,13}^{(l)} + Z_{3,21}^{(l),c}) \right. \\ &\quad - Z_{1,43}^{(l)} Y_4^c \sum_m T_m (Z_{2,4}^{(m)} + Z_{4,2}^{(m)}) \\ &\quad \left. - Z_{2,43}^{(l)} Y_4^c \sum_m T_m (Z_{1,4}^{(m)} + Z_{4,1}^{(m)}) \right] Y_3^c . \end{aligned} \quad (6.3.55)$$

This is the general solution to the problem of finding the nonequilibrium correlator (6.3.45).

In the special case of the circuit shown in Fig. 6.4, if we take the characteristics of nonlinear resistances in the form

$$V_i(I) = R_i I + \frac{1}{2} \alpha_i I^2 \quad (6.3.56)$$

similar to (4.5.14), we will have

$$\begin{aligned} Z_{1,2}^{(1)} &= [(d/dt_1)L + R_1] \delta(t_{12}), \\ Z_{1,2}^{(2)} &= R_2 \delta(t_{12}), \\ Z_{1,23}^{(0)} &= \alpha_1 \delta(t_1, t_2, t_3), \\ Z_{1,2}^c &= [(d/dt_1)L + R_0] \delta(t_{12}), \end{aligned} \quad (6.3.57)$$

where $R_0 = R_1 + R_2$. Since the charge $Q = \int I dt$ is time-reversal invariant, we have

$$\begin{aligned} \varepsilon_1 &= 1, \\ Z_{3,21}^{(0),c} &= \varepsilon_1^3 Z_{1,11}^{(0)}(-t_3, -t_2, -t_1) \\ &= \alpha_1 \delta(t_1, t_2, t_3) . \end{aligned} \quad (6.3.58)$$

From (6.3.55), we obtain the spectral representation

$$\begin{aligned} Y_{12,3}^c &= (2\pi)^{-1/2} k(i\omega_1 L + R_0)^{-1} (i\omega_2 L + R_0)^{-1} \\ &\times \sum_{l=1}^2 \{ 3T_l \alpha_l - 2\alpha_l (T_1 R_1 + T_2 R_2) [(i\omega_2 L + R_0)^{-1} \\ &+ (i\omega_1 L + R_0)^{-1}] \} (-i\omega_3 L + R_0)^{-1} \delta(\omega_1 + \omega_2 + \omega_3). \end{aligned} \quad (6.3.59)$$

Note that here, as always, $Y_{12,3}^c$ in the time representation meets the causality condition

$$Y_{12,3}^c = 0 \quad \text{for } t_3 > \max(t_1, t_2). \quad (6.3.60)$$

This can easily be verified by writing the temporal analogue of (6.3.59) as

$$\begin{aligned} Y_{12,3}^c &= k \int Y(t_{14}) Y(t_{25}) \sum_{l=1}^2 \{ 3T_l \alpha_l \delta(t_{45}) Y(t_{53}) \\ &- 2\alpha_l (T_1 R_1 + T_2 R_2) P_{45} [Y(t_{45}) Y(t_{53})] \} dt_4 dt_5, \end{aligned} \quad (6.3.61)$$

where

$$Y(t) = L^{-1} \exp(-R_0 t/L) \eta(t). \quad (6.3.62)$$

The expression in (6.3.61) corresponding to the first term of the sum P_{45} is zero for $t_3 > t_1$, and the expression corresponding to the second term of that sum is zero for $t_3 > t_2$.

6.3.4 The Threefold Flux Correlator for Serially Connected Nonlinear Subsystems at Different Temperatures

We will sketch the procedure for computing the threefold correlator of the fluxes $J_\alpha = \dot{B}_\alpha$ for the case considered in the previous subsection. In the nonquantum case, from (5.6.54) and (5.6.79), by elimination of L_{123} we obtain

$$Q_1 Q_2 Q_3 G_{123} + P_{(123)} Q_{1,45} Q_2 Q_3 G_{24} G_{35} = Q_{123} + P_{(123)} Q_{12,4} G_4 Q_{43}. \quad (6.3.63)$$

Changing over to $Y_{..}$ and $Z_{..}$ yields

$$Z_1 Z_2 Z_3 Y_{123} + P_{(123)} Z_{1,45} Z_2 Z_3 Y_{24} Y_{35} = Z_{123} + P_{(123)} Z_{12,4} Y_4 Z_{43}. \quad (6.3.64)$$

From this we can find the function $Y_{123} = \langle J_1, J_2, J_3 \rangle$:

$$Y_{123} = Y_1 Y_2 Y_3 (Z_{123} + P_{(123)} Z_{12,4} Y_4 Z_{43} - P_{(123)} Z_{1,45} Y_4 Y_5 Z_{42} Z_{53}). \quad (6.3.65)$$

For nonlinear elements connected in series the functions $Z_{12}, Z_{12,4}, Z_{123}, Z_{1,23}$ should be replaced by the complete functions $Z_{12}^c, Z_{12,4}^c, Z_{123}^c, Z_{1,23}^c = Z_{1,23}^{(1)} + Z_{1,23}^{(2)}$. As a result,

$$\begin{aligned} Y_{123} &= Y_1^c Y_2^c Y_3^c (Z_{123}^c + P_{(123)} Z_{12,4}^c Y_4^c Z_{43}^c \\ &- P_{(123)} Z_{1,45}^c Y_4^c Y_5^c Z_{42}^c Z_{53}^c), \end{aligned} \quad (6.3.66)$$

where $Y_{1,2}^c = (Z_{1,2}^c)^{-1}$; Z_{12}^c and $Z_{12,3}^c$ are given by (6.3.49), and Z_{123}^c by the formula

$$Z_{123}^c = - \sum_{l=1}^2 (kT_l)^2 P_{(123)} (Z_{1,23}^{(l)} + Z_{1,23}^{(l)t.c.}), \quad (6.3.67)$$

which follows from (5.6.102c). This, in principle, solves the problem. The computational formulas with a larger number of serially connected dissipative elements have the same form.

By way of example, consider the circuit shown in Fig. 6.4, for which (6.3.56, 57) hold. Then in the spectral representation,

$$\begin{aligned} Y_{1,2}^c &= f(\omega_1)\delta(\omega_1 + \omega_2), \\ Z_{12}^c &= 2k(T_1R_1 + T_2R_2)\delta(\omega_1 + \omega_2), \\ Z_{1,23}^c &= (2\pi)^{-1/2}(\alpha_1 + \alpha_2)\delta(\omega_1 + \omega_2 + \omega_3), \\ Z_{12,3}^c &= 3(2\pi)^{-1/2}k(T_1\alpha_1 + T_2\alpha_2)\delta(\omega_1 + \omega_2 + \omega_3), \end{aligned} \quad (6.3.68)$$

where $f(\omega) = (i\omega L + R_1 + R_2)^{-1}$, and from (6.3.66, 67) we easily obtain

$$\begin{aligned} Y_{123} &= \langle I(\omega_1), I(\omega_2), I(\omega_3) \rangle \\ &= (2\pi)^{-1/2}S(\omega_1, \omega_2)\delta(\omega_1 + \omega_2 + \omega_3), \end{aligned} \quad (6.3.69)$$

where

$$\begin{aligned} S(\omega_1, \omega_2) &= k^2 f_1 f_2 f_3 [-6(\alpha_1 T_1^2 + \alpha_2 T_2^2) + 6(\alpha_1 T_1 + \alpha_2 T_2) \\ &\quad \times (R_1 T_1 + R_2 T_2)(f_1^* + f_2^* + f_3^*) - 4(\alpha_1 + \alpha_2) \\ &\quad \times (R_1 T_1 + R_2 T_2)^2 (f_1^* f_2^* + f_2^* f_3^* + f_1^* f_3^*)] \end{aligned}$$

and $f_j = f(\omega_j)$.

If the two temperatures T_1 and T_2 were the same, i.e. $T_1 = T_2 = T$, then this correlator could be found using the relation (6.2.9) taken at $s_{111} = 0$, $f_{111} = -(\alpha_1 + \alpha_2)/L$, $d_{11} = (R_1 + R_2)/L$, $r_{11} = 1/L$. We will have

$$\begin{aligned} \langle I(\omega_1)I(\omega_2)I(\omega_3) \rangle &= -6(2\pi)^{-1/2}i(kT)^2 L^3 |f_1 f_2 f_3|^2 \omega_1 \omega_2 \omega_3 \delta(\omega_1 + \omega_2 + \omega_3). \end{aligned} \quad (6.3.70)$$

If $T_1 = T_2 = T$, the same result can be obtained from (6.3.69), as expected.

6.3.5 Nonfluctuational Fluxes in Systems Containing Nonlinear Dissipative Elements at Different Temperatures

If individual quadratic dissipative parts of a complex system have different temperatures, then the system may have relatively weak (of the order of kT) fluxes of internal parameters (not solely thermal fluxes), although no external forces act on the system and the appropriate Onsager cross coefficients $L_{\alpha,\beta} = L_{\beta,\alpha}$ relating the parameters to temperature are zero. These fluxes are caused by detecting the fluctuations. We will concentrate on one specific example of the fluxes, namely the

electric current. The thermoelectric effect described in Sect. 4.4.4 will be assumed absent, which implies that the coefficients (4.4.54) must be zero.

To begin with, we will give a general treatment. According to (5.6.88), i.e.

$$L_1 \equiv \langle \mathcal{E}_1 \rangle_{h=0} = \frac{1}{2} kT Z_{1,23} (Y_{2,3} + Y_{3,2}) = kT Z_{1,23} Y_{2,3} \quad (6.3.71)$$

(nonquantum case), in quadratic dissipative elements ordered thermodynamic forces emerge that oppose the fluctuation detection. When all parts of a system have the same temperature, the above forces and the fluctuation detection are strictly balanced. The balance is disturbed when different nonlinearities have different temperatures.

Let us now generalize (6.3.71) to cover the case of the composite system. The value $L_1 = \langle \mathcal{E}_1 \rangle$ at $h = 0$ is obtained by averaging the stochastic representation of random forces, which according to (5.7.58) and (5.6.98) has, in a linear-quadratic approximation, the form

$$\mathcal{E}_1 = \sum_0 (T_{12}^{(\sigma)} \xi_2^{(\sigma)} + T_{123}^{(\sigma)} \xi_2^{(\sigma)} J_3) \quad (T_{123}^{(\sigma)} p_3 = S_{123}^{(\sigma)}) . \quad (6.3.72)$$

Here $\xi_2^{(\sigma)}$ are random functions with zero mean and correlators $\langle \xi_1^{(\sigma)}, \xi_2^{(\tau)} \rangle = \delta_{\sigma\tau} R_{12}^{(\sigma)}$. In order to obtain L_1 by averaging (6.3.72), we should take into account fluctuations of the current I_3 in a linear approximation, i.e. we should put

$$I_3 = Y_{3,4} \sum_{\tau} T_{45}^{(\tau)} \xi_5^{(\tau)} . \quad (6.3.73)$$

Substituting (6.3.73) into (6.3.72) and averaging gives

$$L_1 = \langle \mathcal{E}_1 \rangle_{h=0} = \sum_{\sigma, \tau} T_{123}^{(\sigma)} T_{45}^{(\tau)} \langle \xi_2^{(\sigma)} \xi_5^{(\tau)} \rangle Y_{3,4} = Z_{14,3}^- Y_{3,4} . \quad (6.3.74)$$

The function $Z_{14,3}^- = \sum_{\sigma} T_{123}^{(\sigma)} T_{45}^{(\sigma)} R_{25}^{(\sigma)}$ is similar to $Q_{14,3}^- = Z_{14,3}^- p_3$ [see (5.6.77)] and, strictly speaking, it is given by the relationship

$$Z_{12,3}^- = kT (Z_{1,23} - Z_{3,12}^{\text{t.c.}}) , \quad (6.3.75)$$

which is equivalent to (5.6.85) taken in the nonquantum form. But, as shown in Sect. 5.6.8, $Z_{3,12}^{\text{t.c.}}$ or $Q_{3,12}^{\text{t.c.}}$ exert no influence on L_1 . After substitution of (6.3.75) into (6.3.74) and omitting the above-mentioned insignificant term, we will obtain (6.3.71). In the case of the complex system that consists of serially connected subsystems, random forces of the type (6.3.72) emerge in each of the subsystems, and the total force is equal to their sum. Therefore, (6.3.72) must be complemented by a summation over subsystems

$$\mathcal{E}_1 = \sum_{m=1}^r \sum_{\sigma} (T_{12}^{(\sigma m)} \xi_2^{(\sigma m)} + T_{123}^{(\sigma m)} \xi_2^{(\sigma m)} J_3) . \quad (6.3.76)$$

In this case, $\langle \xi_1^{(\sigma l)}, \xi_2^{(\tau m)} \rangle = \delta_{\sigma\tau} \delta_{lm} R_{12}^{(\sigma m)}$, and the functions $\xi^{(\sigma m)}$ are mutually uncorrelated (and, in general, they are not correlated to anything that occurred previously). For each subsystem a formula

$$\sum_{\sigma} T_{123}^{(\sigma m)} T_{45}^{(\sigma m)} R_{25}^{(\sigma m)} \equiv Z_{14,3}^{-(m)} = kT Z_{1,43}^{(m)} \quad (6.3.77)$$

of the type (6.3.75) must hold (the term $Z^{t.c.}$ is omitted here). If different subsystems have different temperatures, then these relationships must, of course, include appropriate temperatures:

$$Z_{14,3}^{(m)} = kT_m Z_{1,43}^{(m)}. \quad (6.3.78)$$

As a matter of fact, fluctuations $\xi^{(\sigma m)}$ emerge in the m th subsystem and “do not feel” the temperature and the fluctuations of the other subsystems. Their intensity must only be determined by the temperature of the subsystem in which they are generated. Equation (6.3.73) must contain the complete admittance, i.e. it must have the form

$$I_3 = Y_{3,4}^c \sum_{m\sigma} T_{45}^{(\sigma m)} \xi_5^{(\sigma m)} = \left(\sum_m Z_{3,4}^{(m)} \right)^{-1} \sum_{m\sigma} T_{45}^{(\sigma m)} \xi_5^{(\sigma m)}. \quad (6.3.79)$$

Substituting (6.3.79) into (6.3.76) and averaging, from (6.3.78), we readily obtain

$$\langle \mathcal{E}_1 \rangle = \sum_m \langle \mathcal{E}_1^{(m)} \rangle, \quad (6.3.80)$$

where

$$\langle \mathcal{E}_1^{(m)} \rangle = \frac{1}{2} kT_m Z_{1,23}^{(m)} (Y_{2,3}^c + Y_{3,2}^c) = kT_m Z_{1,23}^{(m)} Y_{2,3}^c. \quad (6.3.81)$$

The quantity (6.3.81) is the mean force in the m th subsystem. The result (6.3.80, 81) is the generalization of (6.3.74, 75) to the case of serially connected subsystems at different temperatures.

We would now like to find the mean flux in the system. If we apply a formula of the type (5.6.26), but written for fluxes and modified admittances, to the entire system, in the absence of external forces, we will have

$$J_1 = Y_{1,2}^c \mathcal{E}_2 + \frac{1}{2} Y_{1,23}^c \mathcal{E}_2 \mathcal{E}_3 \quad (6.3.82)$$

or

$$J_1 = Y_{1,2}^c \left(\mathcal{E}_2 - \frac{1}{2} \sum_m Z_{2,34}^{(m)} Y_3^c Y_4^c \mathcal{E}_2 \mathcal{E}_3 \right). \quad (6.3.83)$$

Averaging gives

$$\langle J_1 \rangle = Y_{1,2}^c \left(\langle \mathcal{E}_2 \rangle - \frac{1}{2} \sum_m Z_{2,34}^{(m)} \langle J_3, J_4 \rangle \right). \quad (6.3.84)$$

The correlator for the fluxes is calculated in a linear approximation:

$$\langle J_3, J_4 \rangle = Y_3^c Y_4^c \sum_l kT_l (Z_{3,4}^{(l)} + Z_{4,3}^{(l)}). \quad (6.3.85)$$

Substituting into (6.3.84) formulas (6.3.80, 81, 85), with (6.3.81) written as

$$\langle \mathcal{E}_1^{(m)} \rangle = kT_m Z_{1,23}^{(m)} Y_2^c Y_3^c Z_{2,3}^c = kT_m Z_{1,23}^{(m)} Y_2^c Y_3^c \sum_l Z_{2,3}^{(l)}, \quad (6.3.86)$$

we obtain

$$\langle J_1 \rangle = k Y_1^c \sum_{ml} Z_{1,23}^{(m)} Y_2^c Y_3^c (T_m - T_l) Z_{2,3}^{(l)}. \quad (6.3.87)$$

Specifically, for the case of two subsystems we will have

$$\langle J_1 \rangle = k(T_1 - T_2) Y_1^c (Z_{1,23}^{(1)} Y_2^c Y_3^c Z_{2,3}^{(2)} - Z_{1,23}^{(2)} Y_2^c Y_3^c Z_{2,3}^{(1)}) . \quad (6.3.88)$$

We thus see that this quantity may be distinct from zero.

6.3.6 An Example of Flux Due to Temperature Difference Between Nonlinear Resistances

Consider the series connection of two RC-circuits shown in Fig. 6.5. The circuits have nonlinear resistances in contact with heat baths at different temperatures.

If we connect an external e.m.f., h , across one RC circuit, as shown in Fig. 6.6, we will have the following equations:

$$I_0 = f_1(h), \quad Q_1/C_1 = h , \quad (6.3.89)$$

where $f(h)$ is the characteristic of the nonlinear resistance and I_0 is the current through it. If we now take it in the form (4.5.1), we will obtain from (6.3.89)

$$I_0 = S_1 h + \frac{1}{2} \gamma_1 h^2, \quad \dot{Q}_1 = C_1 \dot{h} . \quad (6.3.90)$$

The total current I will be

$$I = (S_1 + C_1 d/dt)h + \frac{1}{2} \gamma_1 h^2 . \quad (6.3.91)$$

For one RC-circuit we thus have

$$Y_{1,2}^{(1)} = (S_1 + C_1 d/dt_1) \delta(t_{12}) , \quad (6.3.92a)$$

$$Y_{1,23}^{(1)} = \gamma_1 \delta(t_{12}) \delta(t_{13}) . \quad (6.3.92b)$$

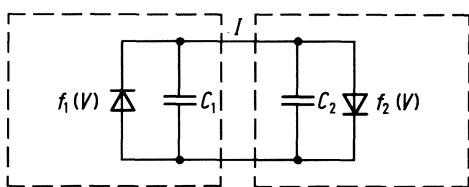


Fig. 6.5. Two serially connected RC-circuits with nonlinear resistances at different temperatures

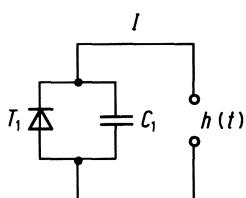


Fig. 6.6. RC-circuit with nonlinear resistor to which an external e.m.f. h is applied

For the diode model of nonlinear resistance discussed in Sects. 3.3.2–4 the characteristic $f_1(V)$, when ignoring the mean e.m.f. arising in the quadratic nonlinearity, has the form

$$f_1(V) = I_1 [\exp(\beta e p_1 V) - \exp(-\beta e q_1 V)] , \quad (6.3.93)$$

as a result of simplifying (3.3.20). From this we can easily find

$$S_1 = \frac{df_1}{dV}(0) = \beta e I_1 , \quad (6.3.94a)$$

$$\gamma_1 = \frac{d^2 f_1}{dV^2}(0) = (\beta e)^2 (p_1^2 - q_1^2) I_1 . \quad (6.3.94b)$$

If we then use a more exact formula (3.3.20), which includes the displacive force, we will have

$$f_1(V) = -\frac{1}{2} \beta e^2 (p_1^2 - q_1^2) I_1 / C_1 + S_1 V + \frac{1}{2} \gamma V^2 , \quad (6.3.95)$$

since the correction is small. We will treat this equation as

$$f_1(V) = S_1(V + \langle \mathcal{E}^{(1)} \rangle) + \frac{1}{2} \gamma(V + \langle \mathcal{E}^{(1)} \rangle)^2 . \quad (6.3.96)$$

Comparison of (6.3.95) with (6.3.96) gives

$$S_1 \langle \mathcal{E}^{(1)} \rangle = -\frac{1}{2} \beta e^2 (p_1^2 - q_1^2) I_1 / C_1 + O(\beta^2 e^4) . \quad (6.3.97)$$

Adding the fluctuational e.m.f. V_f , we will replace (6.3.89) by the formulas $I_0 = f_1(h + V_f)$, $Q_1/C_1 = h + V_f$. Then, from (6.3.96), we will have

$$I = (S_1 + C_1 d/dt)(h + \langle \mathcal{E}^{(1)} \rangle + V_f) + \frac{1}{2} \gamma_1 (h + \langle \mathcal{E}^{(1)} \rangle + V_f)^2 . \quad (6.3.98)$$

This is nothing else but the equation

$$I = Y_{1,2}^{(1)}(h_2 + \mathcal{E}_2^{(1)}) + \frac{1}{2} Y_{1,23}^{(1)}(h_2 + \mathcal{E}_2^{(1)})(h_3 + \mathcal{E}_3^{(1)}) , \quad (6.3.99)$$

which is equivalent to (5.6.26), and so we obtain

$$\mathcal{E}^{(1)} = \langle \mathcal{E}^{(1)} \rangle + V_f . \quad (6.3.100)$$

Using (6.3.94), we can reduce (6.3.97) to the form

$$\langle \mathcal{E}^{(1)} \rangle = -kT\gamma_1/(2S_1 C_1) . \quad (6.3.101)$$

The reason for this shift has been discussed in Sect. 3.3. We will now show that the mean e.m.f. can also be derived from (6.3.71), which can be written as

$$\langle \mathcal{E}_1 \rangle = -\frac{1}{2} k T Z_{1,2} Y_{2,34} (Z_{3,4} + Z_{4,3}) . \quad (6.3.102)$$

From (6.3.92a) the impedance $Z_{3,4}^{(1)} = (Y_{3,4}^{(1)})^{-1}$ in the time representation becomes

$$Z_{3,4}^{(1)} = C_1^{-1} \exp(-st_{34}) \eta(t_{34}) , \quad (6.3.103)$$

where $s = S_1/C_1$. Therefore,

$$Z_{3,4} + Z_{4,3} = C_1^{-1} \exp(-s|t_{34}|) . \quad (6.3.104)$$

From (6.3.92b) we obtain

$$Y_{2,34}(Z_{3,4} + Z_{4,3}) = \gamma_1/C_1 \quad (6.3.105)$$

and hence, by (6.3.102),

$$\langle \mathcal{E}^{(1)} \rangle = -\frac{1}{2}kTC_1^{-1} \int_{-\infty}^{t_1} \exp(-st_{12}) dt_2 \cdot \gamma_1/C_1 = -\frac{1}{2}kT\gamma_1/(S_1 C_1), \quad (6.3.106)$$

which coincides with (6.3.101).

Let us now turn to the composite circuit depicted in Fig. 6.5. We will apply the diode model to each nonlinear resistance. For simplicity, we will suppose that for both RC-circuits the values of capacitances and resistances are the same:

$$C_2 = C_1, \quad (6.3.107a)$$

$$S_2 = S_1. \quad (6.3.107b)$$

For (6.3.107b) to hold at different temperatures, it is necessary that the constants $I_1^{(1)}$ and $I_1^{(2)}$ for different resistances be different since the equation $\beta_1 eI_1^{(1)} = \beta_2 eI_1^{(2)}$ is equivalent to (6.3.107b) due to (6.3.94a). According to (6.3.107), the total impedance $Z_{1,2}^c$ will be twice as large, and the total admittance $Y_{1,2}^c$ half as large as the corresponding function for each circuit. Therefore, from (6.3.88) we have

$$\langle I_1 \rangle = \frac{1}{8}k(T_1 - T_2)(Y_{1,23}^{(1)} - Y_{1,23}^{(2)})Y_2^{(1)}Y_3^{(1)}Z_{2,3}^{(1)} \quad (6.3.108)$$

or

$$\langle I_1 \rangle = -\frac{1}{16}k(T_1 - T_2)(Y_{1,23}^{(1)} - Y_{1,23}^{(2)})(Z_{2,3}^{(1)} + Z_{3,2}^{(1)}). \quad (6.3.109)$$

By (6.3.92b) we have $Y_{1,23}^{(1)} - Y_{1,23}^{(2)} = (\gamma_1 - \gamma_2)\delta(t_1, t_2, t_3)$. The expression on the right-hand side of (6.3.109) is calculated in a similar way to (6.3.105), to yield

$$\langle I_1 \rangle = -\frac{1}{16}k(T_1 - T_2)(\gamma_1 - \gamma_2)C_1^{-1}. \quad (6.3.110)$$

We will now try to account for the result obtained using the concepts of induced charges in the diode model, which lead to the corrected characteristic (3.3.20), and hence to the displacement e.m.f. (6.3.101). In the combined scheme of Fig. 6.5 the effective capacitance will be the total capacitance $C_1 + C_2 = 2C_1$. Therefore, in (3.3.20) and (6.3.101), instead of C_1 we will have to use the total capacitance $2C_1$. As a result, we will have the following mean e.m.f.'s:

$$\langle \mathcal{E}^{(1)} \rangle = -k(4C_1S_1)^{-1}T_1\gamma_1, \quad (6.3.111a)$$

$$\langle \mathcal{E}^{(2)} \rangle = -k(4C_1S_1)^{-1}T_2\gamma_2, \quad (6.3.111b)$$

into which different temperatures enter. Knowing these e.m.f.'s we can find the expression

$$K_1 = \langle \mathcal{E}_1 \rangle - \frac{1}{2} \sum_m Z_{1,23}^{(m)} \langle I_2, I_3 \rangle (\langle \mathcal{E}_1 \rangle = \langle \mathcal{E}^{(1)} \rangle + \langle \mathcal{E}^{(2)} \rangle), \quad (6.3.112)$$

which enters into (6.3.84). From (6.3.85) and the equality $Y_1^c = Y_1^{(1)}/2$, we obtain for the composite system,

$$\begin{aligned} \langle I_2, I_3 \rangle &= \frac{1}{4}k(T_1 + T_2)Y_2^{(1)}Y_3^{(1)}(Z_{2,3}^{(1)} + Z_{3,2}^{(1)}) \\ &= \frac{1}{4}k(T_1 + T_2)(Y_{2,3}^{(1)} + Y_{3,2}^{(1)}). \end{aligned} \quad (6.3.113)$$

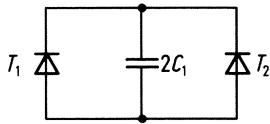


Fig. 6.7. A circuit equivalent to that shown in Fig. 6.5

Therefore,

$$\sum_m Z_{1,23}^{(m)} \langle I_2, I_3 \rangle = -\frac{1}{4}k(T_1 + T_2)Z_1^{(1)}(Y_{1,23}^{(1)} + Y_{1,23}^{(2)})(Z_{2,3}^{(1)} + Z_{3,2}^{(1)}). \quad (6.3.114)$$

Substituting (6.3.111, 114) into (6.3.112) yields

$$\begin{aligned} K_1 &= -k(4C_1S_1)^{-1}(T_1\gamma_1 + T_2\gamma_2) + k(8C_1)^{-1}(T_1 + T_2)Z_1^{(1)}(\gamma_1 + \gamma_2) \\ &= k(8C_1S_1)^{-1}[(T_1 + T_2)(\gamma_1 + \gamma_2) - 2T_1\gamma_1 - 2T_2\gamma_2] \\ &= -k(8C_1S_1)^{-1}(T_1 - T_2)(\gamma_1 - \gamma_2). \end{aligned} \quad (6.3.115)$$

To obtain the mean current $\langle I \rangle$, according to (6.3.84), it remains to operate on (6.3.115) on the left by the admittance $Y_1^c = Y_1^{(1)}/2$. This, due to the fact that (6.3.115) is constant, amounts to multiplying by $S^c = S_1/2$. We thus arrive at (6.3.110).

This result can thus be obtained in terms of the induced charges used in the diode model.

For the mean current (6.3.110) to be nonzero, γ_2 must be different from γ_1 . To obtain the largest current (at fixed temperatures) the nonlinear resistances (detectors) should be aligned so that they face each other, as shown in Fig. 6.7. For the case of equal nonlinearities, $\gamma_1 - \gamma_2$ will then turn into $2\gamma_1$.

As with the thermoelectric current, when a constant current $\langle I \rangle$ flows through the resistances, the cooler resistance heats up and the hotter one cools down, i.e. according to the second law of thermodynamics the ordered energy of electric current is obtained owing to the current-induced heat flow that levels off the temperatures.

6.4 Application of Cubic FDRs to Calculate Non-Gaussian Properties of Flicker Noise

6.4.1 Flicker Noise

Flicker noise is characterized by the fact that the spectral density of fluctuations varies over a wide frequency range as ω^{-1} . The exponent may be slightly different, but in any event the fluctuations grow in intensity with decreasing frequency. Flicker noise occurs widely in a wide variety of systems, and a theoretical understanding is therefore highly desirable. The mechanism of flicker noise is not

yet clear, but, as we will see, one can calculate the non-Gaussian behaviour of flicker noise, namely the threefold and fourfold correlators, while ignoring the specific nature of the mechanism involved.

Flicker noise is characterized not only by a $1/\omega$ -type dependence, but also by the fact that the $1/\omega$ -type part of the spectral density of the fluctuational current is proportional to the square of the average current, if the current is constant. Furthermore, this part was shown to depend on the number of current carriers in a conductor. We now wish to express this mathematically. To begin with, we separate the total spectral density of the fluctuating current into two parts – equilibrium and nonequilibrium parts:

$$S_J(\omega) = S_J(\omega)_0 + S_J^{(2)}(\omega). \quad (6.4.1)$$

Here $S_J(\omega)_0$ is the equilibrium part. It is independent of the average current flowing through the noisy resistor. According to (5.3.92), or rather its nonquantum form, i.e. when $\Theta_2^- = 1$, we have

$$S_J(\omega)_0 = 2kT\text{Re}[Y'(\omega)], \quad (6.4.2)$$

where

$$Y'(\omega) = \int \exp(-i\omega t_{12}) Y(t_1; t_2) dt_{12}. \quad (6.4.3)$$

The second term on the right-hand side of (6.4.1) is the nonequilibrium contribution due to the current. The superscript (2) indicates that it is proportional to the squared average current. Considering also what has been said above about the dependence on the number N of current carriers, we have

$$S_J^{(2)}(\omega) = s^0(\omega) \langle J \rangle^2, \quad (6.4.4)$$

where

$$s^0(\omega) = 2\pi a/(N\omega). \quad (6.4.5)$$

Here we have taken into account that the current $\langle J \rangle$ varies with N at a given voltage. In (6.4.5) $a = 10^{-2} - 10^{-3}$ is a constant known as the Hooge constant [6.1].

Let our resistor with flicker noise have a resistance R . We assume it to be linear, so that the cubic admittance is zero:

$$Y_{1,234} = 0. \quad (6.4.6)$$

At first we connect across the resistor a voltage source with a constant e.m.f. u and zero internal resistance. Then, from (6.4.1, 2, 4) we will have

$$S_J(\omega) = 2kTR^{-1} + s^0(\omega)R^{-2}u^2. \quad (6.4.7)$$

In this case the e.m.f. u plays the role of a force conjugate of the charge Q that has flowed, which is taken to be an internal thermodynamic parameter B_1 . Supposing that the force $h(t) = u(t)$ is variable in time we obtain in a linear–cubic approximation the equation

$$\langle J_1, J_2 \rangle = Y_{12}^0 + \frac{1}{2} Y_{12,34}^0 h_3 h_4, \quad (6.4.8)$$

which can be taken either in the time or spectral representation. The superscript 0 in (6.4.8) shows that the function is concerned with the case where the resistor is connected to nothing but the voltage source.

In the spectral representation (6.4.8) becomes

$$\begin{aligned} S_J(\omega_1)\delta(\omega_1 + \omega_2) &\equiv \langle J(\omega_1), J(\omega_2) \rangle \\ &= Y^0(\omega_1, \omega_2) + \frac{1}{2} \int \int Y^0(\omega_1, \omega_2; \omega_3, \omega_4) h(\omega_3) \\ &\quad \times h(\omega_4) d\omega_3 d\omega_4. \end{aligned} \quad (6.4.9)$$

If we assume $h(t)$ to be constant, i.e. $h(t) = u$, then from the relation

$$h(\omega) = (2\pi)^{-1/2} \int e^{i\omega t} h(t) dt \quad (6.4.10)$$

[see (5.2.13)], we will obtain

$$h(\omega) = (2\pi)^{1/2} u \delta(\omega), \quad (6.4.11)$$

where we have used the integral representation of the delta function. Substituting (6.4.7, 11) into (6.4.9) gives

$$s^0(\omega_1) R^{-2} \delta(\omega_1 + \omega_2) = \pi Y^0(\omega_1, \omega_2; 0, 0). \quad (6.4.12)$$

We see from (6.4.12) that, since $S_J^{(2)}(\omega)$ is proportional to the square of the current, the dependence $1/\omega$ is thus imposed on the biadmittance $Y_{12,34}^0$. The freedom of choice of the biadmittance thus appears to be limited by this formula. Specifically, the biadmittance cannot be zero. It can be said that flicker noise refers to linear-cubic nonequilibrium thermodynamics.

It is important that, when $Y_{12,34}$ is known, we can immediately find threefold and fourfold correlators using (5.4.108b, c), and also using

$$\langle J_1, J_2, J_3 \rangle = Y_{123,4} h_4. \quad (6.4.13)$$

Owing to (6.4.6) all the dissipationally determinable functions vanish, and thus the functions $Y_{123,4}$, Y_{1234} coincide with the dissipationally undeterminable functions $Y_{123,4}^{(2)}$, $Y_{1234}^{(2)}$, which can be computed using (5.4.108b, c).

6.4.2 How Will Flicker Noise Change if a Two-Terminal Impedor Is Connected to a Resistance with Flicker Properties?

Before we proceed to compute threefold and fourfold correlators for one model, we will consider the case where a linear two-terminal impedor that has no flicker properties is connected in series with a “flicker” resistor and a voltage source. We then have the equation

$$\langle J_1, J_2 \rangle = Y_{12} + \frac{1}{2} Y_{12,34} h_3 h_4, \quad (6.4.14)$$

similar to (6.4.8). Here Y_{12} , $Y_{12,34}$ are different from Y_{12}^0 , $Y_{12,34}^0$. The question presents itself of whether it is possible to find $Y_{12,34}$, knowing $Y_{12,34}^0$. This can be done if we take into consideration that $Z_{12,34}$, as with other functions

$Z_{1\dots m, (m+1)\dots n}$ characterizing the statistical behaviour of random forces emerging in the resistor, must remain unchanged when the resistor is connected into various circuits.

Using (5.7.42), we can easily find $Z_{12,34}^{(2)} = Z_1 Z_2 Y_{12,34}^{(2)} Z_3 Z_4$, i.e. in our case,

$$Z^0(-\omega_1, -\omega_2; -\omega_3, -\omega_4) = R^4 Y^0(\omega_1, \omega_2; \omega_3, \omega_4), \quad (6.4.15a)$$

$$\begin{aligned} Z(-\omega_1, -\omega_2; -\omega_3, -\omega_4) \\ = [R + z(\omega_1)][R + z(\omega_2)][R + z(-\omega_3)] \\ \times [R + z(-\omega_4)] Y(\omega_1, \omega_2; \omega_3, \omega_4). \end{aligned} \quad (6.4.15b)$$

Here $z(\omega)$ is the impedance of the connected two-terminal impedor determined by the formula $Z_{1,2} = z(-\omega_1)\delta(\omega_1 + \omega_2)$, which is analogous to (5.2.29). Equating the biimpedances in (6.4.15a, b) gives

$$\begin{aligned} Y(\omega_1, \omega_2; \omega_3, \omega_4) &= [1 + gz(\omega_1)]^{-1} [1 + gz(\omega_2)]^{-1} [1 + gz(-\omega_3)]^{-1} \\ &\times [1 + gz(-\omega_4)]^{-1} Y^0(\omega_1, \omega_2; \omega_3, \omega_4), \end{aligned} \quad (6.4.16)$$

where $g = 1/R$. Substituting this into (6.4.14), we obtain the correlator for the current

$$\begin{aligned} \langle J(\omega_1), J(\omega_2) \rangle &= Y(\omega_1, \omega_2) + \frac{1}{2} \int [1 + gz(\omega_1)]^{-1} [1 + gz(\omega_2)]^{-1} \\ &\times [1 + gz(-\omega_3)]^{-1} [1 + gz(-\omega_4)]^{-1} Y^0(\omega_1, \omega_2; \omega_3, \omega_4) \\ &\times h(\omega_3) h(\omega_4) d\omega_3 d\omega_4. \end{aligned} \quad (6.4.17)$$

Assuming the e.m.f. to be constant, we use (6.4.11) to find from this

$$\begin{aligned} S_J(\omega_1) \delta(\omega_1 + \omega_2) &\equiv \langle J(\omega_1), J(\omega_2) \rangle \\ &= Y(\omega_1, \omega_2) + [1 + gz(\omega_1)]^{-1} [1 + gz(\omega_2)]^{-1} \\ &\times [1 + gz(0)]^{-2} \pi Y^0(\omega_1, \omega_2; 0, 0) u^2. \end{aligned} \quad (6.4.18)$$

Using (6.4.12), we then find

$$S_J^{(2)}(\omega) = |1 + gz(\omega)|^{-2} [1 + gz(0)]^{-2} s^0(\omega) R^{-2} u^2. \quad (6.4.19)$$

If we then take into account the fact that $u/[R + z(0)]$ is nothing but the constant average current, and introduce the function $s(\omega)$ by the formula

$$S_J^{(2)}(\omega) = s(\omega) \langle J \rangle^2, \quad (6.4.20)$$

analogous to (6.4.4), we get

$$s(\omega) = |1 + gz(\omega)|^{-2} s^0(\omega). \quad (6.4.21)$$

6.4.3 Correlators for Flicker Noise in a Model of Fluctuating Resistance

The above reasoning was concerned with the case of arbitrary biadmittances $Y_{12,34}^0$ meeting (6.4.12). Here we will be looking at some specific forms of that function, turning to a model of fluctuating resistance.

From (6.4.4), or rather from the equation

$$\begin{aligned} S_J^{(2)}(\omega) &= s^0(\omega)(u/R)^2 \\ &= s^0(\omega)g^2u^2, \end{aligned} \quad (6.4.22)$$

which holds with the two-terminal impedor $z(\omega)$ disconnected, it is natural to suppose that the flicker part of the current fluctuations is caused by the fluctuations of the resistance R or, equivalently, of the inverse resistance $g = R^{-1}$. In fact, neglecting the equilibrium fluctuations we can write

$$J(t) = g(t)u. \quad (6.4.23)$$

We use this to find, for a constant u , the correlator

$$\langle J(t_1), J(t_2) \rangle^{(2)} = \langle g(t_1), g(t_2) \rangle u^2. \quad (6.4.24)$$

Here subscript (2) implies that the correlator has no equilibrium part. For spectra, this gives

$$S_J^{(2)}(\omega) = S_g(\omega)u^2. \quad (6.4.25)$$

This formula coincides with (6.4.22) if

$$s^0(\omega) = S_g(\omega)/\langle g \rangle^2. \quad (6.4.26)$$

Using

$$\begin{aligned} [R(t)]^{-1} &= [\langle R \rangle + \delta R(t)]^{-1} \\ &= \langle R \rangle^{-1} - \langle R \rangle^{-2} \delta R(t) + \dots, \end{aligned} \quad (6.4.27)$$

we get

$$\begin{aligned} \langle g(t_1), g(t_2) \rangle &= \langle R \rangle^{-4} \langle \delta R(t_1) \delta R(t_2) \rangle \\ &= \langle R \rangle^{-4} \langle R(t_1), R(t_2) \rangle, \end{aligned} \quad (6.4.28)$$

so that $S_g(\omega) = \langle R \rangle^{-4} S_R(\omega)$. Therefore, (6.4.26) can be written as

$$s^0(\omega) = S_R(\omega)/\langle R \rangle^2. \quad (6.4.29)$$

Thus, in the model of fluctuating resistance $s^0(\omega)$ is treated as a dimensionless spectral density of fluctuations of resistance or conductivity of the flicker resistor.

Firstly, we will show that in the model of fluctuating resistance we can easily confirm the formula (6.4.21) obtained by general methods and valid, therefore, for any model.

With the two-terminal impedor connected, instead of (6.4.23) we will have

$$[R(t) + z_0(d/dt)] J(t) = u. \quad (6.4.30)$$

Here the operator $z_0(d/dt)$ describes the influence of the two-terminal impedor; $z_0(p)$ is an appropriately chosen function. It is easy to prove that

$$z_0(i\omega) = z(\omega). \quad (6.4.31)$$

Solving (6.4.30) for the current and using the expansion

$$[\langle R \rangle + z_0(d/dt) + \delta R(t)]^{-1} = [\langle R \rangle + z_0(d/dt)]^{-1} - [\langle R \rangle + z_0(d/dt)]^{-1} \times \delta R(t)[\langle R \rangle + z_0(d/dt)]^{-1} + \dots, \quad (6.4.32)$$

we get

$$J(t) = [\langle R \rangle + z_0(0)]^{-1} u - [\langle R \rangle + z_0(d/dt)]^{-1} \delta R(t)[\langle R \rangle + z_0(0)]^{-1} u. \quad (6.4.33)$$

Here we have taken into account that

$$[\langle R \rangle + z_0(d/dt)]^{-1} u = [\langle R \rangle + z_0(0)]^{-1} u \quad (6.4.34)$$

because the e.m.f. u is constant.

Using (6.4.33) we can easily find the correlator

$$\begin{aligned} \langle J(t_1), J(t_2) \rangle^{(2)} &= [\langle R \rangle + z_0(d/dt_1)]^{-1} [\langle R \rangle + z_0(d/dt_2)]^{-1} \\ &\times \langle R(t_1), R(t_2) \rangle [\langle R \rangle + z_0(0)]^{-2} u^2. \end{aligned} \quad (6.4.35)$$

If we now go over to the spectral densities of fluctuations and take into consideration (6.4.29, 31), we then find (6.4.19) at $g^{-1} = R = \langle R \rangle$. Hence, (6.4.21) follows from (6.4.35).

We now turn to the biadmittance, and hence to the threefold and fourfold correlators. For simplicity, we suppose initially that the two-terminal impedor $z(\omega)$ is not connected to the circuit. Then, ignoring the equilibrium current fluctuations, we will have (6.4.23), or, if we assume that the e.m.f. $h(t) = u(t)$ is not constant, we will have

$$J(t) = g(t)h(t). \quad (6.4.36)$$

Hence,

$$\delta J(t)/\delta h(t') = g(t)\delta(t - t'). \quad (6.4.37)$$

Using (6.4.36) we can write the correlator for the current in the form

$$\langle J(t_1), J(t_2) \rangle = Y^0(t_1, t_2) + \langle g(t_1), g(t_2) \rangle h(t_1)h(t_2) \quad (6.4.38)$$

(time representation). Differentiating this, we easily obtain

$$Y_{12,34}^0 \equiv \frac{\delta^2 \langle J(t_1), J(t_2) \rangle}{\delta h(t_3)\delta h(t_4)} = P_{34} \left\langle \frac{\delta J(t_1)}{\delta h(t_3)}, \frac{\delta J(t_2)}{\delta h(t_4)} \right\rangle \quad (6.4.39)$$

or, owing to (6.4.37),

$$Y^0(t_1, t_2; t_3, t_4) = \langle g(t_1), g(t_2) \rangle [\delta(t_{13})\delta(t_{24}) + \delta(t_{14})\delta(t_{23})]. \quad (6.4.40)$$

We have thus completely determined the biadmittance in the frame of the fluctuating-resistance model. Concerning the result (6.4.40) one observation can be made. If in (6.4.40) instead of the exact function $\delta(\tau)$ we substitute the symmetrical $[\delta_\mu(-\tau) = \delta_\mu(\tau)]$ approximation $\delta_\mu(\tau)$ of that function, which has a finite but small width μ , then this will automatically violate the causality condition of the type

(5.2.6) for μ arbitrarily small. To avoid this, it would be advisable to introduce in (6.4.36) a small delay by putting

$$J(t) = g(t)h(t - \varepsilon), \quad (6.4.41)$$

where ε is a small positive quantity. Then

$$\delta J(t)/\delta h(t') = g(t)\delta(t - t' - \varepsilon) \quad (6.4.42)$$

and instead of (6.4.40) we will have

$$Y^0(t_1, t_2; t_3, t_4) = \langle g(t_1), g(t_2) \rangle P_{34} \delta(t_{13} - \varepsilon) \delta(t_{24} - \varepsilon). \quad (6.4.43)$$

With this admittance, if we replace $\delta(\tau)$ by $\delta_\mu(\tau)$, the causality condition will not be violated if only $\mu \ll \varepsilon$.

In the spectral representation we can manage without distinguishing between (6.4.40) and (6.4.43). In this representation the biadmittance will have the form

$$\begin{aligned} Y^0(\omega_1, \omega_2; \omega_3, \omega_4) &\equiv (2\pi)^{-2} \int \exp(-i\omega_1 t_1 - \dots - i\omega_4 t_4) Y^0(t_1, t_2; t_3, t_4) dt_1 \dots dt_4 \\ &= (2\pi)^{-2} P_{34} \int \exp(-i\omega_1 t_1 - \dots - i\omega_4 t_4) \langle g(t_1)_1, g(t_2) \rangle \\ &\quad \times \delta(t_{13}) \delta(t_{24}) dt_1 \dots dt_4, \end{aligned} \quad (6.4.44)$$

i.e.

$$\begin{aligned} Y^0(\omega_1, \omega_2; \omega_3, \omega_4) &= (2\pi)^{-2} P_{34} \int \exp[-i(\omega_1 + \omega_3)t_1 - i(\omega_2 + \omega_4)t_2] \\ &\quad \times \langle g(t_1), g(t_2) \rangle dt_1 dt_2. \end{aligned} \quad (6.4.45)$$

Hence,

$$Y^0(\omega_1, \omega_2; \omega_3, \omega_4) = (2\pi)^{-1} P_{34} \langle g(\omega_1 + \omega_3), g(\omega_2 + \omega_4) \rangle, \quad (6.4.46)$$

where

$$g(\omega) = (2\pi)^{-1/2} \int e^{-i\omega t} g(t) dt. \quad (6.4.47)$$

Since, by (6.4.26)

$$\begin{aligned} \langle g(\omega), g(\omega') \rangle &= S_g(\omega) \delta(\omega + \omega') \\ &= s^0(\omega) \langle g \rangle^2 \delta(\omega + \omega'), \end{aligned} \quad (6.4.48)$$

the formula (6.4.46) yields

$$\begin{aligned} Y^0(\omega_1, \omega_2; \omega_3, \omega_4) &= (2\pi)^{-1} P_{34} s^0(\omega_1 + \omega_3) \langle g \rangle^2 \delta(\omega_1 + \omega_2 + \omega_3 + \omega_4). \end{aligned} \quad (6.4.49)$$

We can now return to the case where the two-terminal impedor $z(\omega)$ is connected to the flicker resistor. Substituting (6.4.49) into (6.4.16) gives

$$\begin{aligned} Y(\omega_1, \omega_2; \omega_3, \omega_4) = & (2\pi)^{-1} g^2 [1 + gz(\omega_1)]^{-1} [1 + gz(\omega_2)]^{-1} \\ & \times [1 + gz(-\omega_3)]^{-1} [1 + gz(-\omega_4)]^{-1} [s^0(\omega_1 + \omega_3) \\ & + s^0(\omega_1 + \omega_4)] \delta(\omega_1 + \dots + \omega_4), \end{aligned} \quad (6.4.50)$$

where $g = \langle g \rangle$. Note that for the fluctuating-resistance model we can prove (6.4.16), reasoning along the same lines as in deriving (6.4.35). It is necessary merely to write a relation similar to (6.4.33) for the case where the e.m.f. u is not constant.

Knowing the biadmittance (6.4.50) from (5.4.108b, c) and (6.4.13), we can readily obtain the desired fourfold correlator

$$\begin{aligned} \langle J(\omega_1), \dots, J(\omega_4) \rangle = & (kT)^2 \pi^{-1} g^2 \operatorname{Re} P_{(123)} \{ [1 + gz(\omega_1)]^{-1} [1 + gz(\omega_2)]^{-1} \\ & \times [1 + gz^*(\omega_3)]^{-1} [1 + gz^*(\omega_4)]^{-1} [s^0(\omega_1 + \omega_3) \\ & + s^0(\omega_1 + \omega_4)] \} \delta(\omega_1 + \dots + \omega_4) \end{aligned} \quad (6.4.51)$$

and the threefold correlator

$$\begin{aligned} \langle J(\omega_1), J(\omega_2), J(\omega_3) \rangle = & kT (2\pi)^{-1} g^2 P_{(123)} \int [1 + gz(\omega_1)]^{-1} [1 + gz(\omega_2)]^{-1} [1 + gz^*(\omega_3)]^{-1} \\ & \times [1 + gz^*(\omega_4)]^{-1} [s^0(\omega_1 + \omega_3) + s^0(\omega_1 + \omega_4)] \\ & \times \delta(\omega_1 + \dots + \omega_4) u(\omega_4) d\omega_4, \end{aligned} \quad (6.4.52)$$

which characterize the non-Gaussian properties of flicker noise. When writing (6.4.51), we have taken into account that $z^*(\omega) = z(-\omega)$, $s^{0*}(\omega) = s^0(\omega)$. The presence of the function $\delta(\omega_1 + \dots + \omega_4)$ makes the integral with respect to ω_4 in (6.4.52) trivial.

We see that the use of the fluctuating-resistance model enabled us to find the above-mentioned correlators of flicker noise. Owing to the presence of the function $s^0(\omega)$, these correlators contain dependences of the type $(\omega_k + \omega_l)^{-1}$, i.e. dependences of the typically flicker form.

6.4.4 Another Way of Obtaining Correlators

Formulas of the type (6.4.51, 52) can be derived differently by a nonrigorous treatment with the help of the fluctuating-resistance model. Let us now look at the procedure. Suppose, for simplicity, that the two-terminal impedor is purely active. Denoting its resistance by R_0 , we have $z(\omega) = R_0$. At constant R_0 , according to Ohm's law, we have, including the equilibrium fluctuations,

$$J(t) = (R + R_0)^{-1} u(t) + \xi(t), \quad (6.4.53)$$

where $\xi(t)$ is a Gaussian random function with zero mean. According to the formula

$$S_J(\omega)_0 = 2kT(R + R_0)^{-1} \quad (6.4.54)$$

[see (6.4.2)], which describes equilibrium fluctuations, the function has the correlator

$$\langle \xi(t_1) \xi(t_2) \rangle = 2kT(R + R_0)^{-1} \delta(t_{12}). \quad (6.4.55)$$

The random function $\xi(t)$ being Gaussian, the fourfold moment of the current (6.4.53) at $u(t) \equiv 0$ has the form

$$\begin{aligned} & \langle J(t_1) \dots J(t_4) \rangle \\ &= \langle \xi(t_1) \xi(t_2) \rangle \langle \xi(t_3) \xi(t_4) \rangle + \langle \xi(t_1) \xi(t_3) \rangle \langle \xi(t_2) \xi(t_4) \rangle \\ & \quad + \langle \xi(t_1) \xi(t_4) \rangle \langle \xi(t_2) \xi(t_3) \rangle \\ &= 4(kT)^2 (R + R_0)^{-2} [\delta(t_{12}) \delta(t_{34}) + \delta(t_{13}) \delta(t_{24}) \\ & \quad + \delta(t_{14}) \delta(t_{23})]. \end{aligned} \quad (6.4.56)$$

The relations (6.4.54–56) are exact for constant R . Now suppose that this resistance is not constant, due to flicker noise. Since this noise is dominated by slowly varying spectral components, we can assume that the resistance also varies slowly. With a slight sacrifice of rigor we will consider that (6.4.55) holds quasi-statically for the case of the variable resistance:

$$\langle \xi(t_1) \xi(t_2) \rangle_{R(\cdot)} = 2kT[R(t_1) + R_0]^{-1} \delta(t_{12}). \quad (6.4.57)$$

This has not yet been averaged over $R(t)$. Substituting (6.4.57) into (6.4.56) we will have, in this quasi-static approximation,

$$\begin{aligned} \langle J(t_1) \dots J(t_4) \rangle_{R(\cdot)} &= 4(kT)^2 P_{(123)} \{ [R(t_1) + R_0]^{-1} \\ & \quad \times [R(t_3) + R_0]^{-1} \delta(t_{12}) \delta(t_{34}) \}. \end{aligned} \quad (6.4.58)$$

We now average over $R(t)$ using the expansion

$$\begin{aligned} [R(t) + R_0]^{-1} &= [\langle R \rangle + R_0 + \delta R(t)]^{-1} \\ &= (\langle R \rangle + R_0)^{-1} - (\langle R \rangle + R_0)^{-2} \delta R(t) + \dots. \end{aligned} \quad (6.4.59)$$

The dots denote expressions that yield terms of higher order of smallness in kT ; therefore, we will ignore them. The averaging gives

$$\begin{aligned} & \langle J(t_1) \dots J(t_4) \rangle - U \\ &= 4(kT)^2 (\langle R \rangle + R_0)^{-4} \{ \langle R(t_1), R(t_3) \rangle \delta(t_{12}) \delta(t_{34}) \\ & \quad + \langle R(t_1), R(t_2) \rangle [\delta(t_{13}) \delta(t_{24}) \\ & \quad + \delta(t_{14}) \delta(t_{23})] \}, \end{aligned} \quad (6.4.60)$$

where

$$\begin{aligned} U &= 4(kT)^2 (\langle R \rangle + R_0)^{-2} \\ & \times [\delta(t_{12}) \delta(t_{34}) + \delta(t_{13}) \delta(t_{24}) + \delta(t_{14}) \delta(t_{23})]. \end{aligned} \quad (6.4.61)$$

If the correlator (6.4.57) is further averaged over $R(t)$ using (6.4.59), we will have

$$\begin{aligned}\langle J(t_1)J(t_2) \rangle &= \langle \xi(t_1)\xi(t_2) \rangle \\ &= 2kT(\langle R \rangle + R_0)^{-1}\delta(t_{12}).\end{aligned}\quad (6.4.62)$$

Therefore, the expression (6.4.61) is nothing other than

$$P_{(123)}[\langle J(t_1)J(t_2) \rangle \langle J(t_3)J(t_4) \rangle]. \quad (6.4.63)$$

Because at $u = 0$, $\langle J \rangle = 0$, it is this expression that is the difference between the moment $\langle J(t_1) \dots J(t_4) \rangle$ and the correlator $\langle J(t_1), \dots, J(t_4) \rangle$. Therefore the expressions on the right- and left-hand side of (6.4.60) are equal to the correlator $\langle J(t_1), \dots, J(t_4) \rangle$. Equating the right-hand side to this correlator and going over to the spectral representation, we obtain from (6.4.60) via (6.4.29)

$$\begin{aligned}\langle J(\omega_1), \dots, J(\omega_4) \rangle &= 2\pi^{-1}(kT)^2\langle R \rangle^2(\langle R \rangle + R_0)^{-4}[s^0(\omega_1 + \omega_2) + s^0(\omega_1 + \omega_3) \\ &\quad + s^0(\omega_1 + \omega_4)]\delta(\omega_1 + \dots + \omega_4).\end{aligned}\quad (6.4.64)$$

Exactly the same result follows from (6.4.51) at $z(\omega) = R_0$.

Let us now proceed to compute the threefold correlator, supposing $u(t)$ to be nonzero. Multiplying expressions of the type (6.4.53) taken at a nonconstant $R(t)$ and keeping only the terms linear in $u(t)$, we find

$$\begin{aligned}\langle J(t_1)J(t_2)J(t_3) \rangle_{R(\cdot)} &= P_{(123)}\{\langle \xi(t_1)\xi(t_2) \rangle [R(t_3) + R_0]^{-1}u(t_3)\}\end{aligned}\quad (6.4.65)$$

or, substituting the quasi-static formula (6.4.57),

$$\begin{aligned}\langle J(t_1)J(t_2)J(t_3) \rangle_{R(\cdot)} &= 2kTP_{(123)}\{[R(t_1) + R_0]^{-1}[R(t_3) + R_0]^{-1}\delta(t_{12})u(t_3)\}.\end{aligned}\quad (6.4.66)$$

Averaging further over $R(t)$ using (6.4.59), we get

$$\begin{aligned}\langle J(t_1)J(t_2)J(t_3) \rangle - V &= 2kT(\langle R \rangle + R_0)^{-4}P_{(123)}[\langle R(t_1), R(t_3) \rangle \delta(t_{12})u(t_3)],\end{aligned}\quad (6.4.67)$$

where

$$V = 2kT(\langle R \rangle + R_0)^{-2}P_{(123)}[\delta(t_{12})u(t_3)]. \quad (6.4.68)$$

If we take into account

$$\begin{aligned}\langle J(t_1), J(t_2) \rangle_0 &= \langle \xi(t_1)\xi(t_2) \rangle \\ &= 2kT(\langle R \rangle + R_0)^{-1}\delta(t_{12}),\end{aligned}\quad (6.4.69)$$

which now holds instead of (6.4.62), and also the equation

$$\langle J(t) \rangle = (\langle R \rangle + R_0)^{-1}u(t), \quad (6.4.70)$$

which can be obtained from (6.4.53) by averaging over $\xi(t)$ and $R(t)$, we can easily

see that the expression (6.4.68) only differs from

$$\begin{aligned} & \langle J(t_1)J(t_2)J(t_3) \rangle - \langle J(t_1), J(t_2), J(t_3) \rangle \\ & = P_{(123)}[\langle J(t_1), J(t_2) \rangle \langle J(t_3) \rangle] + \langle J(t_1) \rangle \langle J(t_2) \rangle \langle J(t_3) \rangle \end{aligned} \quad (6.4.71)$$

by the terms of the order of uuu , which we ignore. Hence, in our approximation (6.4.67) is the same as the correlator $\langle J(t_1), J(t_2), J(t_3) \rangle$. With this in mind, we go over in (6.4.67) to the spectral representation. Substituting

$$u(t) = (2\pi)^{-1/2} \int \exp(-i\omega_4 t) u(\omega_4) d\omega_4 \quad (6.4.72)$$

into (6.4.67) and considering that

$$J(\omega) = (2\pi)^{-1/2} \int e^{-i\omega t} J(t) dt, \quad (6.4.73)$$

we obtain, from (6.4.67),

$$\begin{aligned} & \langle J(\omega_1), J(\omega_2), J(\omega_3) \rangle \\ & = \pi^{-1} k T R^2 (R + R_0)^{-4} \int [P_{(123)} s^0(\omega_1 + \omega_2)] \\ & \quad \times \delta(\omega_1 + \dots + \omega_4) u(\omega_4) d\omega_4. \end{aligned} \quad (6.4.74)$$

It is this formula that follows from (6.4.52) if we substitute $z(\omega) = R_0$.

6.4.5 The Fourfold Correlator of Flicker Noise Applied to the Theory of the Voss and Clark Experiment

We will begin with considering the nonrigorous arguments that led to the above-mentioned experiment [6.2]. It is well known that equilibrium fluctuations are described in terms of spectral density, determined by the exact formula (6.4.2). Suppose that an additional nonflicker resistance R_0 is connected in series with the flicker resistor. We further suppose that there is no external e.m.f. u , and that the resistance undergoes slow fluctuations $R = R(t)$. If now we generalize (6.4.54) to this case in a nonrigorous way, we obtain

$$S_J(\omega, t) = 2kT[R(t) + R_0]^{-1}; \quad (6.4.75)$$

whence, the spectral density of the voltage V across the resistor R_0 is

$$S_V(\omega, t) = 2kT[R(t) + R_0]^{-1} R_0^2. \quad (6.4.76)$$

Our adding of the argument t in S_J and S_V signifies that the spectral density now becomes time-dependent. Selecting some frequency interval $(\omega_1, \omega_2) = (\omega_1, \omega_1 + \Delta\omega)$ and introducing the quantity

$$P(t) = S_V(\omega_1, t) \Delta\omega, \quad (6.4.77)$$

we will find, from (6.4.76), that the spectral density of this quantity must depend on

frequency as $1/\omega$. In fact, substituting (6.4.76) into (6.4.77) and taking into consideration (6.4.59, 29), we obtain

$$P(t) = 2kTR_0^2(\langle R \rangle + R_0)^{-1} \Delta\omega - 2kTR_0^2(\langle R \rangle + R_0)^{-2} \delta R(t) \Delta\omega , \quad (6.4.78a)$$

$$\begin{aligned} S_P(\omega) &= 4(kT)^2 R_0^4 (\langle R \rangle + R_0)^{-4} (\Delta\omega)^2 S_R(t) \\ &= 4(kT)^2 R_0^4 \langle R \rangle^2 (\langle R \rangle + R_0)^{-4} \Delta\omega^2 s^0(\omega) . \end{aligned} \quad (6.4.78b)$$

This result suggests the idea of forming the empirical spectral density of flicker noise or a quantity of the type (6.4.77) by means of devices and, having measured its spectral density, to verify the dependence $1/\omega$. This was done in [6.2] and this dependence was indeed found for sufficiently small frequencies.

Since (6.4.75) is only an intuitive, unjustified formula (in the case of nonconstant R), a more justified theory of this experiment is required. We can see from the very beginning that the experimentally measurable spectral density $S_P(\omega)$ is a linear transformation of the equilibrium fourfold moment $\langle J_1 J_2 J_3 J_4 \rangle$, since the empirical spectral density $S_V(\omega, t)$ and the empirical quantity $P(t)$ must be quadratic in J . However, the fourfold moment consists of two parts, Gaussian and non-Gaussian

$$\langle J_1 \dots J_4 \rangle = P_{(123)}(\langle J_1 J_2 \rangle \langle J_3 J_4 \rangle) + \langle J_1, \dots, J_4 \rangle , \quad (6.4.79)$$

the Gaussian part being due to equilibrium fluctuations and free of $1/\omega$ -type flicker dependences. The experimentally found dependence $1/\omega$ is thus due to the correlator $\langle J_1, J_2, J_3, J_4 \rangle$ alone, i.e. due to the non-Gaussian properties of flicker noise.

Let us take a closer look at some of the transformations that occur in the experiment. At first, a voltage V from R_0 is fed to the amplifier and band-pass filter. The latter singles out the spectral components contained within the frequency interval (ω_1, ω_2) . These transformations are linear and they can be described by

$$y(t) = \int D(t - t') V(t') dt' \quad (6.4.80)$$

or spectrally by

$$y(\omega) = F(\omega) V(\omega), \quad F(\omega) = \int e^{-i\omega\tau} D(\tau) d\tau . \quad (6.4.81)$$

The signal is squared,

$$z(t) = y^2(t) , \quad (6.4.82)$$

and averaged over time,

$$P(t) = T_0^{-1} \int_{t-T_0}^t z(t') dt' , \quad (6.4.83a)$$

$$P(\omega) = (i\omega T_0)^{-1} [1 - \exp(-i\omega T_0)] z(\omega) \equiv \Phi(\omega) z(\omega) . \quad (6.4.83b)$$

Finally, we measure the spectral density of the last quantity. We get

$$S_P(\omega) = |\Phi(\omega)|^2 S_z(\omega) , \quad (6.4.84)$$

where

$$|\Phi(\omega)|^2 = \frac{4}{\omega^2 T_0^2} \sin^2 \frac{\omega T_0}{2}. \quad (6.4.85)$$

Since the spectral representation of (6.4.82) has the form

$$z(\omega) = (2\pi)^{-1/2} \int y(v) y(\omega - v) dv, \quad (6.4.86)$$

we can easily find, using (6.4.81, 83b),

$$\begin{aligned} \langle P(\omega_1) P(\omega_2) \rangle &= (2\pi)^{-1} \Phi(\omega_1) \Phi(\omega_2) \int dv_1 dv_2 F(v_1) F(\omega_1 - v_1) \\ &\quad \times F(v_2) F(\omega_2 - v_2) \langle V(v_1) V(\omega_1 - v_1) \\ &\quad \times V(v_2) V(\omega_2 - v_2) \rangle. \end{aligned} \quad (6.4.87)$$

We now take into account that

$$\langle P(\omega_1) P(\omega_2) \rangle = S_P(\omega_1) \delta(\omega_1 + \omega_2) \quad \text{for } \omega_1 \neq 0, \quad (6.4.88a)$$

$$\begin{aligned} \langle V(\omega_1) \dots V(\omega_4) \rangle &= \langle V(\omega_1), \dots, V(\omega_4) \rangle + \text{G.t.} \\ &= S_V(\omega_1, \omega_2, \omega_3) \delta(\omega_1 + \dots + \omega_4) + \text{G.t.}, \end{aligned} \quad (6.4.88b)$$

where G.t. stands for the Gaussian terms that describe equilibrium fluctuations; they are of no interest to us here and are therefore ignored. Using (6.4.88a, b), equation (6.4.87) gives

$$\begin{aligned} S_P(\omega) &= (2\pi)^{-1} |\Phi(\omega)|^2 \int dv_1 dv_2 F(v_1) F(\omega - v_1) F(v_2) F(-\omega - v_2) \\ &\quad \times S_V(v_1, \omega - v_1, v_2). \end{aligned} \quad (6.4.89)$$

From (6.4.64) [or from (6.4.51) at $z(\omega) = R_0$] we have

$$\begin{aligned} S_V(\omega_1, \omega_2, \omega_3) &= 2\pi^{-1} (kT)^2 R^2 R_0^4 (R + R_0)^{-4} \\ &\quad \times [s^0(\omega_1 + \omega_2) + s^0(\omega_1 + \omega_3) + s^0(\omega_2 + \omega_3)]. \end{aligned} \quad (6.4.90)$$

Substituting this into (6.4.89) gives

$$\begin{aligned} S_P(\omega) &= \pi^{-2} (kT)^2 R^2 R_0^4 (R + R_0)^{-4} |\Phi(\omega)|^2 \\ &\quad \times [|K(\omega)|^2 s^0(\omega) + 2 \int f(\omega, \omega') s^0(\omega') d\omega'], \end{aligned} \quad (6.4.91)$$

where

$$K(\omega) = \int F(\omega - v) F(v) dv, \quad (6.4.92a)$$

$$\begin{aligned} f(\omega, \omega') &= f(\omega', \omega) \\ &= \int F(v) F(\omega - v) F(\omega' - v) F(v - \omega - \omega') dv. \end{aligned} \quad (6.4.92b)$$

Compare the final formula (6.4.91) with the nonrigorous formula (6.4.78b). In so doing, we should take into account that $\Delta\omega$ must be interpreted as $(2\pi)^{-1} K(0)$, since, as can be easily seen,

$$\begin{aligned}\langle P(t) \rangle &= \langle y^2(t) \rangle \\ &= (2\pi)^{-1} \int |F(\omega)|^2 S_V(\omega) d\omega \\ &\approx S_V(\omega_1) \cdot (2\pi)^{-1} \int |F(v)|^2 dv.\end{aligned}\tag{6.4.93}$$

Remember that earlier we supposed that $P = S_V \Delta\omega$ [see (6.4.77)]. The comparison suggests firstly that the time averaging (6.4.83a), described by $\Phi(\omega)$, is unnecessary since it only enhances the difference between the expressions being compared. Secondly, the proportionality between $S_P(\omega)$ and $s^0(\omega)$ is distorted by the factor $|K(\omega)|^2/K^2(0)$, which appears in (6.4.91). Suppose, for example, that

$$F(\omega) = \begin{cases} c & \text{for } \omega_1 < |\omega| < \omega_2, \\ 0 & \text{elsewhere.} \end{cases}\tag{6.4.94}$$

This factor will then become

$$|K(\omega)|^2/K^2(0) = (\omega_2 - \omega_1 - |\omega|)^2/(\omega_2 - \omega_1)^2.\tag{6.4.95}$$

Thirdly, in (6.4.91) another term appeared that is due to flicker noise. Its dependence on ω is given by the integral $\int f(\omega, \omega') s^0(\omega') d\omega'$. We see that this dependence differs markedly from the dependence $1/\omega$.

6.5 Notes on References to Chapter 6

The general formulas determining correlators and their derivatives for the Markov systems were found in [6.3] (the three-subscript formulas) and in [6.4] (the four-subscript formulas). In these works, in contrast to Sect. 6.1, the Markov methods were applied and some examples of applications of the above general formulas were also given. In some other works, for instance in [6.5], the correlators were computed by using less systematic Markov methods. The fourfold correlator of an electric field in a boundless medium with cubic nonlinearity was found in [6.6] with the help of non-Markov FDRs. Another example of their application can be found in [6.7]. The possibility of the emergence of an electric current in a passive circuit having no thermoelectric properties, due only to the difference between the temperatures of nonlinear resistances, was pointed out in [6.8]. There the mean current was calculated for the circuit containing two detectors orientated in opposite directions. The fourfold correlator of flicker noise was obtained in [6.9].

Appendices

A1. Relation of Conjugate Potentials in the Limit of Small Fluctuations

According to (2.2.86), we have a relationship of the type

$$\exp(-\kappa^{-1}\Phi) = \int \exp[\kappa^{-1}(Bx - \Psi(B))] dB. \quad (\text{A1.1})$$

We will evaluate this integral by the saddle-point or steepest descent method. Let A be a point at which the integrand is maximal, i.e. at which $\Psi(B) - Bx$ has a minimum. The extremum condition has the form

$$\partial\Psi(B)/\partial B = x. \quad (\text{A1.2})$$

We will assume that this equation has a single root $B^0(x)$ and that the matrix of second derivatives is positive definite:

$$\psi_{\alpha\beta} \equiv \frac{\partial^2 \Psi}{\partial \beta_\alpha \partial \beta_\beta}(B^0) = \text{pos. def.}, \quad (\text{A1.3})$$

so that the extremum corresponds to the minimum of the function $\Psi(B) - Bx$. Expanding it into a Taylor series about the minimum gives

$$\begin{aligned} \Psi(B) - Bx &= \Psi(B^0) - B^0x + \frac{1}{2}\psi_{\alpha\beta}z_\alpha z_\beta + \frac{1}{6}\psi_{\alpha\beta\gamma}z_\alpha z_\beta z_\gamma \\ &\quad + \frac{1}{24}\psi_{\alpha\beta\gamma\delta}z_\alpha z_\beta z_\gamma z_\delta + \dots, \end{aligned} \quad (\text{A1.4})$$

where $z_\alpha = B_\alpha - B_\alpha^0$; $\alpha = 1, \dots, r$. Hence,

$$\begin{aligned} \exp\left[-\frac{1}{\kappa}(\Psi - Bx)\right] &= \exp[-\kappa^{-1}(\Psi(B^0) - B^0x)] \\ &\quad \times \left[1 - \frac{1}{6\kappa}\psi_{\alpha\beta\gamma}z_\alpha z_\beta z_\gamma - \frac{1}{24\kappa}\psi_{\alpha\beta\gamma\delta}z_\alpha z_\beta z_\gamma z_\delta + O(z^5)\right] \\ &\quad \times \exp[-(2\kappa)^{-1}\psi_{\alpha\beta}z_\alpha z_\beta]. \end{aligned} \quad (\text{A1.5})$$

Substituting (A1.5) into (A1.1) gives

$$\begin{aligned} \exp(-\kappa^{-1}\Phi) &= C \exp[\kappa^{-1}(\Psi(B^0) + B^0x)] \\ &\quad \times \left[1 - \frac{1}{6\kappa}\psi_{\alpha\beta\gamma}\langle z_\alpha z_\beta z_\gamma \rangle - \frac{1}{24\kappa}\psi_{\alpha\beta\gamma\delta}\langle z_\alpha z_\beta z_\gamma z_\delta \rangle + \dots\right], \end{aligned} \quad (\text{A1.6})$$

where

$$C = \det^{-1/2} \|\psi_{\alpha\beta}/(2\pi\kappa)\| \quad (\text{A1.7})$$

and the angle brackets $\langle \dots \rangle$ denote averaging with the Gaussian probability density

$$w_0(z) = C^{-1} \exp[-(2\kappa)^{-1} \psi_{\alpha\beta} z_\alpha z_\beta]. \quad (\text{A1.8})$$

This gives zero mean and the correlator $\langle z_\alpha, z_\beta \rangle = \kappa \psi_{\alpha\beta}^{-1}$. Hence,

$$\begin{aligned} \langle z_\alpha z_\beta z_\gamma \rangle &= 0, \\ \langle z_\alpha z_\beta z_\gamma z_\delta \rangle &= \kappa^2 (\psi_{\alpha\beta}^{-1} \psi_{\gamma\delta}^{-1} + \psi_{\alpha\gamma}^{-1} \psi_{\beta\delta}^{-1} + \psi_{\alpha\delta}^{-1} \psi_{\beta\gamma}^{-1}). \end{aligned} \quad (\text{A1.9})$$

Therefore, taking the logarithm, we find from (A1.6)

$$\begin{aligned} \Phi(x) &= \Psi[B^0(x)] - B^0(x)x + \frac{1}{2}\kappa \ln \det \|\psi_{\alpha\beta}/(2\pi\kappa)\| \\ &\quad + \frac{1}{8}\kappa^2 \psi_{\alpha\beta\gamma\delta} \psi_{\alpha\beta}^{-1} \psi_{\gamma\delta}^{-1} + O(\kappa^3). \end{aligned} \quad (\text{A1.10})$$

If in (A1.10) we discard the terms that are small at small κ , we will get $\Phi(x) = \Psi(B^0) - B^0 x$, which, by (A1.2), means that $\Phi(x)$ is the Legendre transform of $\Psi(B)$. The remaining terms in (A1.10) indicate the accuracy of the approximation. We can omit the denominator $2\pi\kappa$ of the fraction at the logarithm sign, since it does not affect the value of derivatives of $\Phi(x)$. Instead of $\ln \det \|\psi_{\alpha\beta}\|$ we can write $\text{Tr} \{\ln \|\psi_{\alpha\beta}\|\}$.

A2. On the Theory of Infinitely Divisible Probability Densities

A2.1 Justification of the Representation (2.4.9) Subject to (2.4.10)

Taking the logarithm of (2.4.3) yields

$$\ln \Theta(iu) = n \ln \Theta_n(iu) = n \ln \{1 + [\Theta_n(iu) - 1]\}. \quad (\text{A2.1})$$

Let us now estimate $\Theta_n(iu) - 1$. By the first equality (A2.1),

$$\Theta_n(iu) - 1 = \exp \left[\frac{\ln \Theta(iu)}{n} \right] - 1 = \sum_{k=1}^{\infty} \frac{1}{k!} \left\{ \frac{\ln \Theta(iu)}{n} \right\}^k. \quad (\text{A2.2})$$

Clearly, at large n (A2.2) is small, or rather has order of magnitude $O(n^{-1})$. Hence, we can write

$$\ln [1 + (\Theta_n(iu) - 1)] = \Theta_n(iu) - 1 + O(n^{-2}),$$

so that from (A2.1) we obtain

$$\ln \Theta(iu) = n [\Theta_n(iu) - 1] + O(n^{-1}). \quad (\text{A2.3})$$

If now we substitute (2.4.2) into the right-hand side of (A2.3), we have

$$\ln \Theta(iu) = n \int \{\exp(iu\eta) - 1\} w_n(\eta) d\eta + O(n^{-1}) \quad \left(u\eta = \sum_{\alpha} u_{\alpha} \eta_{\alpha} \right). \quad (\text{A2.4})$$

This equation can also be written as

$$\ln \Theta(iu) = niu_\alpha(m_n)_\alpha + n \int [\exp(iu\eta) - 1 - iu\eta] w_n(\eta) d\eta + O(n^{-1}), \quad (\text{A2.5})$$

where

$$(m_n)_\alpha = \int \eta_\alpha w_n(\eta) d\eta = m_\alpha/n, \quad m_\alpha = \int \xi_\alpha w(\xi) d\xi. \quad (\text{A2.6})$$

If we denote

$$g_n(\eta) = nn^2 w_n(\eta) \geq 0, \quad (\text{A2.7})$$

then (A2.5) becomes

$$\ln \Theta(iu) = iu_\alpha m_\alpha + \int [\exp(iu\eta) - 1 - iu\eta] \eta^{-2} g_n(\eta) d\eta + O(n^{-1}). \quad (\text{A2.8})$$

According to (2.4.1) and (2.1.6), we obtain

$$-\sum_\alpha \partial^2 \ln \Theta(iu)/\partial u_\alpha^2 = \sum_\alpha \langle \xi_\alpha, \xi_\alpha \rangle \quad \text{for } u = 0. \quad (\text{A2.9})$$

If now we differentiate (A2.8) twice with respect to u_α , sum over α and let $u = 0$, we obtain

$$\sum_\alpha \langle \xi_\alpha, \xi_\alpha \rangle = \int g_n(\eta) d\eta + O(n^{-1}) \quad (\text{A2.10})$$

using (A2.9). It follows from (2.4.8) that $\sum_\alpha \langle \xi_\alpha, \xi_\alpha \rangle < \infty$. Therefore, due to (A2.10) we have

$$\int g_n(\eta) d\eta < \infty. \quad (\text{A2.11})$$

It follows from (A2.7, 11) that the prelimiting function $g_n(\eta)$ satisfies the conditions that the integral be nonnegative and limited, which are similar to (2.4.10). To obtain (2.4.9) from (A2.8) we merely have to approach the limit $n \rightarrow \infty$. As a result, (A2.7) will become $g(\eta)$, which may well contain some singularities of the same type as that of the generalized functions. As to the above conditions, the limiting function naturally resembles the prelimiting function, i.e. for $g(\eta)$ the conditions (2.4.10) are met. It can be expected that the above-mentioned singularities are confined purely to singularities of the type of the conventional and refined delta function to be described below.

A2.2 Example: Gaussian Distribution

Consider Gaussian random variables characterized by means $\langle \xi_\alpha \rangle$ and correlators $s_{\alpha\beta} = \langle \xi_\alpha, \xi_\beta \rangle$. For simplicity, we will assume that the means are zero, and that the matrix of the correlators obeys

$$\sum_\alpha s_{\alpha\alpha} = 1. \quad (\text{A2.12})$$

These conditions can always be met with the help of a shift transformation and rescaling, so that these conditions do not involve any limitations of generality. Of more importance is another accepted condition – the condition that the matrix $s_{\alpha\beta}$ be nondegenerate. If the matrix is degenerate, then some of the variables can be expressed through others. By eliminating them we can obtain a nondegenerate matrix with a smaller number of variables.

For the random variables in question we have $\ln \Theta(iu) = -s_{\alpha\beta}u_\alpha u_\beta/2$. We will now try to represent this expression in the form (2.4.9). Expanding the integrand in (2.4.9) into a series in iuz , we have

$$\ln \Theta(iu) = \int \left[\frac{i^2}{2} u_\alpha u_\beta z_\alpha z_\beta + \frac{i^3}{6} u_\alpha u_\beta u_\gamma z_\alpha z_\beta z_\gamma + \dots \right] z^{-2} g(z) dz . \quad (\text{A2.13})$$

The function $g(z)$ must be such that in the brackets in (A2.13) the terms with $u_\alpha u_\beta u_\gamma$, and hence with $z_\alpha z_\beta z_\gamma$, vanish. This strongly suggests that $g(z)$ must be proportional to the delta function: $g(z) = C\delta(z)$. The constant C can be found from the condition (A2.12), which takes the form

$$\int g(z) dz = 1 \quad (\text{A2.14})$$

owing to a relationship of the type (A2.10) but written for the limiting function $g(z)$. Hence, $C = 1$. Substituting $g(z) = \delta(z)$ into (A2.13) gives

$$\ln \Theta(iu) = -\frac{1}{2} u_\alpha u_\beta \int \frac{z_\alpha}{z} \frac{z_\beta}{z} \delta(z) dz . \quad (\text{A2.15})$$

This integral has an indeterminacy of the type 0/0. To remove this uncertainty, we should clarify the concept of the delta function. By definition, it has the property

$$\int f(z) \delta(z) dz = f(0) \quad (\text{A2.16})$$

for any $f(z)$ among a sufficiently wide variety of functions.

In generalized polar coordinates, this becomes

$$\int f(\rho \mathbf{m}) \bar{\delta}(\rho) d\rho \frac{d\Omega}{c_r} = f(0) \int \frac{d\Omega}{c_r} = f(0) , \quad (\text{A2.17})$$

where $\rho = |z|$, m_α are the components of a unit vector as functions of the angles:

$$m_1 = \cos \vartheta, \quad m_2 = \sin \vartheta \cos \varphi, \quad m_3 = \sin \vartheta \sin \varphi \cos \psi, \dots ; \quad (\text{A2.18})$$

$d\Omega$ is an element of the r -dimensional solid angle, and

$$c_r = \int d\Omega = \begin{cases} r\pi^r/v! & \text{for } r = 2v, \\ \pi^v v! 2^r/(r-1)! & \text{for } r = 2v+1 \end{cases} \quad (\text{A2.19})$$

is the complete r -dimensional solid angle. On the left-hand side of (A2.17) $\bar{\delta}(\rho) = c_r \delta(\rho \mathbf{m}) \rho^{r-1}$ is a one-dimensional delta function.

For a multidimensional space we will introduce a refined, namely isotropic, delta function $\delta_{is}(z)$ by requiring that, in addition to (A2.16, 17), it obeys

$$\int f\left(z, \frac{z}{z}\right) \delta_{is}(z) dz = \int f(0, \mathbf{m}) \frac{d\Omega}{c_r} \quad (\text{A2.20})$$

at any $f(z, \mathbf{m})$. If $p(\mathbf{m})$ is the probability density of \mathbf{m} obeying

$$p(\mathbf{m}) \geq 0, \quad \int p(\mathbf{m}) d\Omega = 1, \quad (\text{A2.21})$$

then

$$\delta(z, z/z) = c_r p(z/z) \delta_{is}(z) \quad (\text{A2.22})$$

will be an anisotropic refined delta function. For this, in place of (A2.20), we will have

$$\begin{aligned} \int f\left(z, \frac{z}{z}\right) \delta\left(z, \frac{z}{z}\right) dz &= c_r \int f\left(z, \frac{z}{z}\right) p\left(\frac{z}{z}\right) \delta_{is}(z) dz \\ &= \int f(0, \mathbf{m}) p(\mathbf{m}) d\Omega. \end{aligned} \quad (\text{A2.23})$$

We will treat $\delta(z)$ in (A2.15) as an anisotropic function (A2.22). Then (A2.15) will be

$$\frac{1}{2} s_{\alpha\beta} u_\alpha u_\beta = \frac{1}{2} u_\alpha u_\beta \int m_\alpha m_\beta p(\mathbf{m}) d\Omega \quad (\text{A2.24})$$

by (A2.23). For this to hold, we will have to select a probability density such that

$$\int m_\alpha m_\beta p(\mathbf{m}) d\Omega = s_{\alpha\beta}. \quad (\text{A2.25})$$

To find $p(\mathbf{m})$ with appropriate properties and also to represent the refined delta function (A2.22) in the form of the limit of conventional functions, requires the theory set forth in Sect. A2.1, according to which $g(z)$ is

$$g(z) = \lim_{n \rightarrow \infty} g_n(z). \quad (\text{A2.26})$$

The prelimiting probability density $w_n(z)$ has zero means and the correlation matrix $s_{\alpha\beta}/n$. It is written as

$$w_n(z) = (2\pi)^{-r/2} n^{r/2} \det^{-1/2} \|s_{\alpha\beta}\| \exp(-\frac{1}{2} ns_{\alpha\beta}^{-1} z_\alpha z_\beta) \quad (\text{A2.27})$$

and obeys

$$\int z_\alpha z_\beta w_n(z) dz = s_{\alpha\beta}/n. \quad (\text{A2.28})$$

Using (A2.7), we obtain from (A2.27) the prelimiting function

$$g_n(z) = (2\pi)^{-r/2} n^{r/2+1} \det^{-1/2} \|s_{\alpha\beta}\| z^2 \exp(-\frac{1}{2} ns_{\alpha\beta}^{-1} z_\alpha z_\beta), \quad (\text{A2.29})$$

which, by (A2.28) and (A2.12), obeys

$$\int g_n(z) dz = 1 . \quad (\text{A2.30})$$

According to (A2.26), as $n \rightarrow \infty$ the function (A2.29) becomes concentrated at $z = 0$ and in the limit yields the delta function (A2.22). But the distribution over the angles

$$p(\mathbf{m}) = \int_0^\infty w_n(\rho \mathbf{m}) \rho^{r-1} d\rho \quad (\text{A2.31})$$

corresponding to (A2.29) is independent of n , and so remains unchanged in the limit. Substitution of (A2.27) into (A2.31) gives

$$p(\mathbf{m}) = \frac{1}{2} \pi^{-r/2} \Gamma(r/2) (\det^{-1/2} \| s_{\alpha\beta} \|) (s_{\alpha\beta}^{-1} m_\alpha m_\beta)^{-r/2} . \quad (\text{A2.32})$$

From the normalization condition for $w_n(z)$, which can be presented as

$$\int w_n(\rho \mathbf{m}) \rho^{r-1} d\rho d\Omega = 1 , \quad (\text{A2.33})$$

and from (A2.31) we obtain the normalization condition (A2.21) for (A2.32). Furthermore, from (A2.7, 28) we get in the limit $n \rightarrow \infty$:

$$\int g_n(z) z_\alpha z_\beta z^{-2} dz = \int g_n(\rho \mathbf{m}) m_\alpha m_\beta \rho^{r-1} d\rho d\Omega = s_{\alpha\beta} \quad (\text{A2.34})$$

for any n . It follows from this and the equation $g(\rho \mathbf{m}) = p(\mathbf{m}) \delta_{is}(\rho \mathbf{m})$ that the density (A2.32) obeys (A2.25).

To sum up, in this Gaussian case the representation (2.4.9) holds for $g(z)$ equal to the refined delta function (A2.22), where the probability density $p(\mathbf{m})$ has the form (A2.32).

A3. Some Formulas Concerning Operator Commutation

We will now apply the formula (3.2.48), which is essentially a Taylor expansion, to the function $\varphi(y) = f(y)\psi(y)$, where $f(y)$, $\psi(y)$ are arbitrary functions. This gives

$$\exp(v\partial/\partial y)[f(y)\psi(y)] = f(y+v)\psi(y+v) \quad (v\partial/\partial y = v_\alpha \partial/\partial y_\alpha) \quad (\text{A3.1})$$

or

$$\exp(v\partial/\partial y)[f(y)\psi(y)] = f(y+v)[\exp(v\partial/\partial y)\psi(y)] . \quad (\text{A3.2})$$

Since ψ is arbitrary, (A3.2) is equivalent to the operator formula

$$\exp(v\partial/\partial y)f(y) = f(y+v)\exp(v\partial/\partial y) , \quad (\text{A3.3})$$

where y is thought of as the operator of multiplication by y . The operators $\partial/\partial y_\alpha$, y_β in (A3.3) obey

$$\frac{\partial}{\partial y_\alpha} y_\beta = y_\beta \frac{\partial}{\partial y_\alpha} + \delta_{\alpha\beta}. \quad (\text{A3.4})$$

An identical commutation relation holds for $-y_\alpha$ and $\partial/\partial y_\beta$. Therefore, in analogy with (A3.3), the following equation must hold:

$$\exp(-vy)f(\partial/\partial y) = f(\partial/\partial y + v)\exp(-vy). \quad (\text{A3.5})$$

In fact, the shift of the argument of f in (A3.3) and (A3.5) is exceptionally due to the operators being noncommutative, the pair $\partial/\partial y$, y having the same noncommutativity as $-y$, $\partial/\partial y$.

Now let a function $f(\xi, \eta)$ be given by the Fourier integral

$$f(\xi, \eta) = \int \exp(iu_\alpha \xi_\alpha) g(u, \eta) du. \quad (\text{A3.6})$$

Instead of ξ we will substitute the vector $\partial/\partial y$ acting to the left of $y \equiv \eta$. By (A3.6), we will have

$$N_{\partial, y} f(\partial/\partial y, y) = \int \exp(iu_\alpha \partial/\partial y_\alpha) g(u, y) du. \quad (\text{A3.7})$$

Applying (A3.3), we thus obtain

$$N_{\partial, y} f(\partial/\partial y, y) = \int g(u, y + iu) \exp(iu_\alpha \partial/\partial y_\alpha) du. \quad (\text{A3.8})$$

The operators $\partial/\partial y$ and y on the right-hand side of (A3.8) act in the reverse order to that on the left-hand side. Introducing the symbol $N_{y, \partial}$ for reverse operator ordering, we have

$$N_{\partial, y} f(\partial/\partial y, y) = N_{y, \partial} \bar{f}(\partial/\partial y, y), \quad (\text{A3.9})$$

where

$$\bar{f}(\xi, \eta) = \int g(u, \eta + iu) \exp(iu\xi) du. \quad (\text{A3.10})$$

The last equation can be written as

$$\bar{f}(\xi, \eta) = \int g\left(u, \eta + \frac{\partial}{\partial \xi}\right) \exp(iu\xi) du \quad (\text{A3.11})$$

or

$$\bar{f}(\xi, \eta) = \exp\left(\sum_\alpha \frac{\partial^2}{\partial \xi_\alpha \partial \eta_\alpha}\right) \int g(u, \eta) \exp(iu\xi) du, \quad (\text{A3.12})$$

since

$$g\left(u, \eta + \frac{\partial}{\partial \xi}\right) = \exp\left(\sum_\alpha \frac{\partial^2}{\partial \xi_\alpha \partial \eta_\alpha}\right) g(u, \eta). \quad (\text{A3.13})$$

Here we have again used (3.2.48). If we now take into account (A3.6), then, from (A3.12), we will arrive at

$$\bar{f}(\xi, \eta) = \exp\left(\sum_{\alpha} \frac{\partial^2}{\partial \xi_{\alpha} \partial \eta_{\alpha}}\right) f(\xi, \eta). \quad (\text{A3.14})$$

If $f(\xi, \eta)$ cannot be represented as the Fourier integral (A3.4), then it can be regarded as a limit of the functions that can be represented by the Fourier integral. Equations (A3.9, 14) hold for prelimiting functions, hence they will hold for the limiting function as well.

A4. Approximate Computation of Derivatives of $\Phi(x)$

The function $\Phi(x)$ is given by (4.2.2), or by (A1.1) at $\Psi(B) = F(B)$. Using (A1.10) gives

$$\Phi(x) = F[B^0(x)] - xB^0(x) + \frac{1}{2}kT \operatorname{Tr} \ln \|F_{\alpha\beta}\| + O((kT)^2), \quad (\text{A4.1})$$

where $F_{\alpha\beta} = \partial^2 F / \partial B_{\alpha} \partial B_{\beta}$ at $B = B^0(x)$, $B^0(x)$ being given by

$$\partial F(B) / \partial B_{\alpha} = x_{\alpha} \quad \text{for } B = B^0(x). \quad (\text{A4.2})$$

Let us take the differential of (A4.1) with respect to x . Using (A4.2), we will obtain

$$d\Phi = -B^0(x)dx + \frac{1}{2}kT d\operatorname{Tr} \ln \|F_{\alpha\beta}\| + O((kT)^2). \quad (\text{A4.3})$$

But

$$d\operatorname{Tr} \ln \hat{M} = \operatorname{Tr}(\hat{M}^{-1} d\hat{M}), \quad (\text{A4.4})$$

therefore

$$d\Phi = -B_{\alpha}^0(x)dx_{\alpha} + \frac{1}{2}kT F_{\alpha\beta}^{-1} dF_{\beta\alpha} + O((kT)^2). \quad (\text{A4.5})$$

We have

$$dF_{\beta\alpha} = \frac{\partial^3 F(B^0(x))}{\partial B_{\beta} \partial B_{\alpha} \partial B_{\gamma}} dB_{\gamma}^0(x) = F_{\beta\alpha\gamma} \frac{\partial B_{\gamma}^0}{\partial x_{\delta}} dx_{\delta}. \quad (\text{A4.6})$$

But the dependence $B^0(x)$ is the inverse of $x = \partial F(B^0) / \partial B^0$, hence

$$\partial B_{\gamma}^0 / \partial x_{\delta} = F_{\gamma\delta}^{-1}. \quad (\text{A4.7})$$

Equations (A4.5–7) yield

$$d\Phi = -B_{\alpha}^0 dx_{\alpha} + \frac{1}{2}kT F_{\alpha\beta}^{-1} F_{\alpha\beta\gamma} F_{\gamma\delta}^{-1} dx_{\delta} + O((kT)^2). \quad (\text{A4.8})$$

Hence

$$\partial \Phi / \partial x_{\delta} = -B_{\delta}^0(x) + \frac{1}{2}kT F_{\delta\gamma}^{-1} F_{\gamma\alpha\beta} F_{\alpha\beta}^{-1} + O((kT)^2). \quad (\text{A4.9})$$

A5. The Contribution of Individual Terms of the Master Equation

Let us denote

$$V_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} = \frac{\partial^{m+n} V(y, B)}{\partial y_{\alpha_1} \dots \partial y_{\alpha_m} \partial B_{\beta_1} \dots \partial B_{\beta_n}} \quad \text{for } y = 0, B = 0. \quad (\text{A5.1})$$

If we now represent the kinetic potential $V(y, B)$ as a Taylor series with the coefficients (A5.1) and substitute it into (3.1.11), we will obtain the following form of the master equation

$$\frac{\partial w}{\partial t} = \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} \frac{(-1)^m}{m! n!} (kT)^{m-1} \frac{\partial^m}{\partial B_{\alpha_1} \dots \partial B_{\alpha_m}} [V_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} B_{\beta_1} \dots B_{\beta_n} w]. \quad (\text{A5.2})$$

We assume that $\partial F(A)/\partial A_\alpha = 0$ at $A = 0$ (this assumption stems from the appropriate selection of the origin of coordinates in space A). Then, from the equation $\kappa_\alpha(0) = 0$ [see (4.1.10)], it follows that the quantities

$$V_\alpha = \left. \frac{\partial V}{\partial y_\alpha} \right|_{y=0, B=0} \quad (\text{A5.3})$$

are small. In fact, by virtue of the equation $\kappa_\alpha(0) = 0$ they are equal to zero in the asymptotic approximation when $V(y, B) = R(y, \partial F(B)/\partial B)$. We believe that the image $R(y, x)$ has a purely macroscopic character, its coefficients being independent of the small parameter kT . Then the coefficients (A5.1) of the kinetic potential will have a weak dependence on kT . The quantities V_α have thus the order $o(1)$. Moreover, using (4.3.31) and (4.3.2), we can see that

$$V_\alpha = O(kT). \quad (\text{A5.4})$$

To get a clearer indication of the magnitude of the terms in (A5.2), we will change the scale of the variables B_α , by introducing the quantities $z_\alpha = B_\alpha/\mu$ proportional to them, where μ is a number to be explained below. Substituting $B_\alpha = \mu z_\alpha$ into (A5.2) gives

$$\begin{aligned} \frac{\partial w}{\partial t} &= \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} \frac{(-1)^m}{m! n!} (kT)^{m-1} \mu^{n-m} \frac{\partial^m}{\partial z_{\alpha_1} \dots \partial z_{\alpha_m}} \\ &\quad \times (V_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} z_{\beta_1} \dots z_{\beta_n} w). \end{aligned} \quad (\text{A5.5})$$

To specify μ we will require that the terms with $m = 1, n = 1$ and with $m = 2, n = 0$ have the same order of smallness. Hence, $1 = kT\mu^{-2}$. Accordingly,

$$\mu = (kT)^{1/2}. \quad (\text{A5.6})$$

For this μ , the quantities z_α have a variance of the order of unity. Using (A5.6), we obtain from (A5.5)

$$\begin{aligned}
\frac{\partial w}{\partial t} = & - \frac{\partial}{\partial z_\alpha} \left[\left(\mu^{-1} V_\alpha + V_{\alpha,\beta} z_\beta + \frac{\mu}{2} V_{\alpha,\beta\gamma} z_\beta z_\gamma + \frac{\mu^2}{6} V_{\alpha,\beta\gamma\delta} z_\beta z_\gamma z_\delta \right) w \right] \\
& + \frac{1}{2} \frac{\partial^2}{\partial z_\alpha \partial z_\beta} \left[\left(V_{\alpha\beta} + \mu V_{\alpha\beta,\gamma} z_\gamma + \frac{\mu^2}{2} V_{\alpha\beta,\gamma\delta} z_\gamma z_\delta \right) w \right] \\
& - \frac{1}{6} \frac{\partial^3}{\partial z_\alpha \partial z_\beta \partial z_\gamma} [(\mu V_{\alpha\beta\gamma} + \mu^2 V_{\alpha\beta\gamma,\delta} z_\delta) w] \\
& + \frac{1}{24} \frac{\partial^4}{\partial z_\alpha \partial z_\beta \partial z_\gamma \partial z_\delta} (\mu^2 V_{\alpha\beta\gamma\delta} w) + O(\mu^3). \tag{A5.7}
\end{aligned}$$

It follows that all three-subscript terms are of order μ , all the four-subscript terms are of order μ^2 . The same is true of the higher terms ignored in (A5.7): all the five-subscript terms have the order μ^3 , and so on. The term V_α/μ , which stands apart, according to (A5.4) has order μ , i.e. in its order it should be classed with the three-subscript terms.

All these features of (A5.7) enable us to construct various approximate equations:

(a) Linear approximation. Permitting the error $O(\mu)$ we have

$$\frac{\partial w}{\partial t} = - \frac{\partial}{\partial z_\alpha} (V_{\alpha,\beta} z_\beta w) + \frac{1}{2} \frac{\partial^2}{\partial z_\alpha \partial z_\beta} (V_{\alpha\beta} w) \tag{A5.8}$$

or, returning again to B ,

$$\frac{\partial w}{\partial t} = - \frac{\partial}{\partial B_\alpha} (V_{\alpha,\beta} B_\beta w) + \frac{1}{2} \mu^2 V_{\alpha\beta} \frac{\partial^2 w}{\partial B_\alpha \partial B_\beta}. \tag{A5.9}$$

Comparison with (2.3.24) and account of the order of magnitude of the terms of the expansion (A5.7) discarded to derive the last equation shows that

$$\begin{aligned}
K_\alpha(B) &= V_{\alpha,\beta} B_\beta + O(\mu^2 V_{\alpha,\beta\gamma} z_\beta z_\gamma) = V_{\alpha,\beta} B_\beta + O(\mu^2), \\
K_{\alpha\beta}(B) &= kT V_{\alpha\beta} + \mu^2 O(\mu V_{\alpha\beta,\gamma} z_\gamma) = kT V_{\alpha\beta} + \mu^2 O(\mu)
\end{aligned} \tag{A5.10}$$

for $B \sim \mu$. To simplify the accuracy estimates in (A5.10), we will put

$$\begin{aligned}
K_\alpha(B) &= V_{\alpha,\beta} B_\beta + O(kT), \\
K_{\alpha\beta}(B) &= kT V_{\alpha\beta} + O(kT)
\end{aligned} \tag{A5.11}$$

(b) Linear-quadratic approximation. Here we should retain in (A5.7) the terms of order μ to obtain

$$\begin{aligned}
\frac{\partial w}{\partial t} = & - \frac{\partial}{\partial z_\alpha} \left[\left(\mu^{-1} V_\alpha + V_{\alpha,\beta} z_\beta + \frac{\mu}{2} V_{\alpha,\beta\gamma} z_\beta z_\gamma \right) w \right] \\
& + \frac{1}{2} \frac{\partial^2}{\partial z_\alpha \partial z_\beta} [(V_{\alpha\beta} + \mu V_{\alpha\beta,\gamma} z_\gamma) w] - \frac{1}{6} \frac{\partial^3}{\partial z_\alpha \partial z_\beta \partial z_\gamma} (\mu V_{\alpha\beta\gamma} w). \tag{A5.12}
\end{aligned}$$

Transferring here to the variables B yields

$$\begin{aligned} K_\alpha(B) &= V_\alpha + V_{\alpha,\beta}B_\beta + \frac{1}{2}V_{\alpha,\beta\gamma}B_\beta B_\gamma + O(\mu^3), \\ K_{\alpha\beta}(B) &= \mu^2(V_{\alpha\beta} + V_{\alpha\beta,\gamma}B_\gamma) + \mu^2O(\mu^2), \\ K_{\alpha\beta\gamma}(B) &= \mu^4V_{\alpha\beta\gamma} + \mu^3O(\mu^2). \end{aligned} \quad (\text{A5.13})$$

Hence,

$$\begin{aligned} K_\alpha(B) &= V_\alpha + V_{\alpha,\beta}B_\beta + \frac{1}{2}V_{\alpha,\beta\gamma}B_\beta B_\gamma + O((kT)^{3/2}), \\ K_{\alpha\beta}(B) &= [kT(V_{\alpha\beta} + V_{\alpha\beta,\gamma}B_\gamma)][1 + O(kT)], \\ K_{\alpha\beta\gamma}(B) &= (kT)^2V_{\alpha\beta\gamma}[1 + O((kT)^{1/2})]. \end{aligned} \quad (\text{A5.14})$$

(c) Linear–quadratic–cubic approximation. In this case, we keep the terms that are written out in (A5.7). Changing to B , we get

$$\begin{aligned} K_\alpha(B) &= V_\alpha + V_{\alpha,\beta}B_\beta + \frac{1}{2}V_{\alpha,\beta\gamma}B_\beta B_\gamma + \frac{1}{6}V_{\alpha,\beta\gamma\delta}B_\beta B_\gamma B_\delta + O(\mu^4), \\ K_{\alpha\beta}(B) &= \mu^2(V_{\alpha\beta} + V_{\alpha\beta,\gamma}B_\gamma + \frac{1}{2}V_{\alpha\beta,\gamma\delta}B_\gamma B_\delta) + \mu^2O(\mu^3), \\ K_{\alpha\beta\gamma}(B) &= \mu^4(V_{\alpha\beta\gamma} + V_{\alpha\beta\gamma,\delta}B_\delta) + \mu^3O(\mu^3), \\ K_{\alpha\beta\gamma\delta}(B) &= \mu^6V_{\alpha\beta\gamma\delta} + \mu^4O(\mu^3). \end{aligned} \quad (\text{A5.15})$$

Therefore,

$$\begin{aligned} K_\alpha(B) &= V_\alpha + V_{\alpha,\beta}B_\beta + \frac{1}{2}V_{\alpha,\beta\gamma}B_\beta B_\gamma + \frac{1}{6}V_{\alpha,\beta\gamma\delta}B_\beta B_\gamma B_\delta + O((kT)^2), \\ K_{\alpha\beta}(B) &= kT(V_{\alpha\beta} + V_{\alpha\beta,\gamma}B_\gamma + \frac{1}{2}V_{\alpha\beta,\gamma\delta}B_\gamma B_\delta)[1 + O((kT)^{3/2})], \\ K_{\alpha\beta\gamma}(B) &= (kT)^2(V_{\alpha\beta\gamma} + V_{\alpha\beta\gamma,\delta}B_\delta)[1 + O(kT)] \\ K_{\alpha\beta\gamma\delta}(B) &= (kT)^3V_{\alpha\beta\gamma\delta}[1 + O((kT)^{1/2})]. \end{aligned} \quad (\text{A5.16})$$

It follows from (A5.14, 16) that $K_\alpha(B)$ in the linear–quadratic approximation and $K_\alpha(B)$, $K_{\alpha\beta}(B)$ in the linear–quadratic–cubic approximation call for a higher relative accuracy: their relative uncertainty must be $o(kT)$, whereas other functions have the larger relative uncertainty $O(kT)$ or $O((kT)^{1/2})$.

A6. Spectral Densities and Related Formulas

A6.1. Definition of Many-Fold Spectral Densities

If there are random functions $\xi_1(t), \xi_2(t), \dots, \xi_r(t)$, then the appropriate random spectra will be given by

$$\xi_\alpha(\omega) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} \exp(-i\omega t) \xi_\alpha(t) dt. \quad (\text{A6.1})$$

This transformation is unitary. Assuming that the random processes are

stationary and stationarily connected, we will define the spectral density $S_{\alpha_1 \dots \alpha_s}(\omega_1, \dots, \omega_{s-1})$ by

$$\langle \xi_{\alpha_1}(\omega_1), \dots, \xi_{\alpha_s}(\omega_s) \rangle = S_{\alpha_1 \dots \alpha_s}(\omega_1, \dots, \omega_{s-1}) \delta(\omega_1 + \dots + \omega_s). \quad (\text{A6.2})$$

It follows from (A6.1) that

$$\begin{aligned} & \langle \xi_{\alpha_1}(\omega_1), \dots, \xi_{\alpha_s}(\omega_s) \rangle \\ &= (2\pi)^{-s/2} \int \exp\left(-i \sum_{\alpha=1}^s \omega_{\alpha} t_{\alpha}\right) \langle \xi_{\alpha_1}(t_1), \dots, \xi_{\alpha_s}(t_s) \rangle dt_1 \dots dt_s. \end{aligned} \quad (\text{A6.3})$$

This suggests that the spectral densities are related to the correlators in the temporal representation by

$$\begin{aligned} & S_{\alpha_1 \dots \alpha_s}(\omega_1, \dots, \omega_{s-1}) \\ &= (2\pi)^{1-s/2} \int \exp\left(-i \sum_{\alpha=1}^{s-1} \omega_{\alpha} t_{\alpha s}\right) \langle \xi_{\alpha_1}(t_1), \dots, \xi_{\alpha_s}(t_s) \rangle dt_1 \dots dt_{s-1}. \end{aligned} \quad (\text{A6.4})$$

($t_{\alpha s} = t_{\alpha} - t_s$). Specifically,

$$S_{\alpha\beta}(\omega) = \int_{-\infty}^{\infty} \exp(-i\omega t_{12}) \langle \xi_{\alpha}(t_1), \xi_{\beta}(t_2) \rangle dt_{12}. \quad (\text{A6.5})$$

A6.2 Space–Time Spectral Densities

When random functions are dependent not only on time, but also on the three-dimensional position vector \mathbf{r} , the random spectra are defined as follows:

$$\xi_{\alpha}(\mathbf{k}, \omega) = (2\pi)^{-2} \int \exp(-i\omega t + i\mathbf{k}\mathbf{r}) \xi_{\alpha}(\mathbf{r}, t) dt d\mathbf{r}. \quad (\text{A6.6})$$

In this case, the spectral densities $S_{\alpha_1 \dots \alpha_s}(\mathbf{k}_1, \omega_1, \dots, \mathbf{k}_{s-1}, \omega_{s-1})$ will be defined by

$$\begin{aligned} & \langle \xi_{\alpha_1}(\mathbf{k}_1, \omega_1), \dots, \xi_{\alpha_s}(\mathbf{k}_s, \omega_s) \rangle \\ &= S_{\alpha_1 \dots \alpha_s}(\mathbf{k}_1, \omega_1, \dots, \mathbf{k}_{s-1}, \omega_{s-1}) \delta(\mathbf{k}_1 + \dots + \mathbf{k}_s) \delta(\omega_1 + \dots + \omega_s). \end{aligned} \quad (\text{A6.7})$$

In analogy with (A6.4), we can now derive similar expressions relating the spectral density to the space–time correlator:

$$\begin{aligned} & S_{\alpha_1 \dots \alpha_s}(\mathbf{k}_1, \omega_1, \dots, \mathbf{k}_{s-1}, \omega_{s-1}) \\ &= (2\pi)^{4-2s} \int \exp\left[-i \sum_{\alpha=1}^{s-1} (\omega_{\alpha} t_{\alpha s} - \mathbf{k}_{\alpha} \mathbf{r}_{\alpha s})\right] \\ & \times \langle \xi_{\alpha_1}(\mathbf{r}_1, t_1), \dots, \xi_{\alpha_s}(\mathbf{r}_s, t_s) \rangle d\mathbf{r}_{1s} dt_{1s} \dots d\mathbf{r}_{s-1,s} dt_{s-1,s}. \end{aligned} \quad (\text{A6.8})$$

Putting $s = 2$, we get

$$S_{\alpha\beta}(\mathbf{k}, \omega) = \int \exp[-i(\omega t_{12} - \mathbf{k}\mathbf{r}_{12})] \langle \xi_{\alpha}(\mathbf{r}_1, t_1), \xi_{\beta}(\mathbf{r}_2, t_2) \rangle dt_{12} d\mathbf{r}_{12}. \quad (\text{A6.9})$$

A6.3 Spectral Density of Spatial Spectra and Space–Time Spectral Density

For the fields $\xi_\alpha(\mathbf{r}, t)$, we may use the expression

$$\xi_{\alpha k}(t) = (2\pi)^{-3/2} \int \exp(i\mathbf{k}\mathbf{r}) \xi_\alpha(\mathbf{r}, t) d\mathbf{r}, \quad (\text{A6.10})$$

which is similar to (4.4.114), to define their random spatial spectra. According to (A6.5) with (α, k) substituted for α , the spectra (A6.10) will have the spectral density

$$S_{\alpha_1 k_1, \alpha_2 k_2}(\omega) = \int \exp(-i\omega t_{12}) \langle \xi_{\alpha_1 k_1}(t_1), \xi_{\alpha_2 k_2}(t_2) \rangle dt_{12}. \quad (\text{A6.11})$$

To work out the relationship between (A6.11) and (A6.9), we will substitute (A6.10) into (A6.11):

$$\begin{aligned} S_{\alpha_1 k_1, \alpha_2 k_2}(\omega) &= (2\pi)^{-3} \int \exp(-i\omega t_{12} + i\mathbf{k}_1 \mathbf{r}_1 + i\mathbf{k}_2 \mathbf{r}_2) \\ &\quad \times \langle \xi_{\alpha_1}(\mathbf{r}_1, t_1), \xi_{\alpha_2}(\mathbf{r}_2, t_2) \rangle d\mathbf{r}_1 d\mathbf{r}_2 d\omega. \end{aligned} \quad (\text{A6.12})$$

We denote

$$\mathbf{k}_{12} = \mathbf{k}_1 - \mathbf{k}_2, \quad \mathbf{k}_0 = \frac{1}{2}(\mathbf{k}_1 + \mathbf{k}_2), \quad \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2, \quad \mathbf{r}_0 = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2). \quad (\text{A6.13})$$

It is easily verified that we will then have

$$\mathbf{k}_1 \mathbf{r}_1 + \mathbf{k}_2 \mathbf{r}_2 = 2\mathbf{k}_0 \mathbf{r}_0 + \frac{1}{2} \mathbf{k}_{12} \mathbf{r}_{12}. \quad (\text{A6.14})$$

We will now substitute this into (A6.12), take notice of the fact that $d\mathbf{r}_1 d\mathbf{r}_2 = d\mathbf{r}_0 d\mathbf{r}_{12}$ and carry out the integration at first with respect to \mathbf{r}_0 . For spatially homogeneous fluctuations this integral becomes trivial, and yields a delta function, since the correlator in (A6.12) is independent of \mathbf{r}_0 . But the integral with respect to \mathbf{r}_{12} and t_{12} is taken using (A6.9). We thus arrive at

$$S_{\alpha k_1, \beta k_2}(\omega) = S_{\alpha\beta}(\frac{1}{2}\mathbf{k}_{12}, \omega) \delta(\mathbf{k}_1 + \mathbf{k}_2). \quad (\text{A6.15})$$

Instead of $S_{\alpha\beta}(\mathbf{k}_{12}/2, \omega)$ we can substitute here $S_{\alpha\beta}(\mathbf{k}_1, \omega)$.

A6.4 Spectral Density of Nonstationary and Nonhomogeneous Random Functions

If a process $\xi(t)$ is not stationary, then we may introduce the time-dependent spectral density

$$S_{\alpha\beta}(\omega, t_0) = \int \exp(-i\omega t) \langle \xi_\alpha(t_0 + t/2), \xi_\beta(t_0 - t/2) \rangle dt. \quad (\text{A6.16})$$

This equation is a generalization of (A6.5) and goes over into it for stationary processes. Substituting into (A6.16) the expression

$$\langle \xi_\alpha(t_1), \xi_\beta(t_2) \rangle = (2\pi)^{-1} \int \exp(i\omega_1 t_1 + i\omega_2 t_2) \langle \xi_\alpha(\omega_1), \xi_\beta(\omega_2) \rangle d\omega_1 d\omega_2 \quad (\text{A6.17})$$

which follows from (A6.1) and changing the integration variables, we will have

$$\begin{aligned} S_{\alpha\beta}(\omega, t_0) &= (2\pi)^{-1} \int \exp[i(v - \omega)t + i\omega_0 t_0] \\ &\quad \times \langle \xi_\alpha(\omega_0/2 + v), \xi_\beta(\omega_0/2 - v) \rangle d\omega_0 dv dt . \end{aligned} \quad (\text{A6.18})$$

To begin with, we will integrate with respect to t to obtain $\delta(v - \omega)$. Integrating then with respect to v , we will obtain

$$S_{\alpha\beta}(\omega, t_0) = \int \exp(i\omega_0 t_0) \langle \xi_\alpha(\omega_0/2 + \omega), \xi_\beta(\omega_0/2 - \omega) \rangle d\omega_0 . \quad (\text{A6.19})$$

In an analogous way, we may introduce the space-time spectral density for a nonstationary and nonhomogeneous random function. This spectral density is defined as

$$\begin{aligned} S_{\alpha\beta}(\mathbf{k}, \omega, \mathbf{r}_0, t_0) &= \int \exp(-i\omega t + ik\mathbf{r}) \langle \xi_\alpha(\mathbf{r}_0 + \mathbf{r}/2, t_0 + t/2), \xi_\beta(\mathbf{r}_0 - \mathbf{r}/2, t_0 - t/2) \rangle d\mathbf{r} dt . \end{aligned} \quad (\text{A6.20})$$

Following along the same lines, we can use this expression to express the spectral density in terms of the correlator of spectra

$$\begin{aligned} S_{\alpha\beta}(\mathbf{k}, \omega, \mathbf{r}_0, t_0) &= \int \exp(i\omega_0 t_0 - ik_0 \mathbf{r}_0) \\ &\quad \times \langle \xi_\alpha(\mathbf{k}_0/2 + \mathbf{k}, \omega_0/2 + \omega), \xi_\beta(\mathbf{k}_0/2 - \mathbf{k}, \omega_0/2 - \omega) \rangle d\mathbf{k}_0 d\omega_0 . \end{aligned} \quad (\text{A6.21})$$

One would be well-advised to use the generalization (A6.16, 20) of the concept of spectral density to the case of nonstationary and nonhomogeneous processes, when the nonstationarity and nonhomogeneity are relatively small. This implies that the correlator

$$\langle \xi_\alpha(\mathbf{r}_0 + \frac{1}{2}\mathbf{r}, t_0 + \frac{1}{2}t), \xi_\beta(\mathbf{r}_0 - \frac{1}{2}\mathbf{r}, t_0 - \frac{1}{2}t) \rangle \quad (\text{A6.22})$$

must vary with \mathbf{r}_0 much more slowly than with \mathbf{r} , and with t_0 much more slowly than with t .

A7. Stochastic Equations for the Markov Process

A7.1 The Ito Stochastic Equation

Solving the Langevin-type equations for a Markov process $y(t)$, we can find appropriate moments or correlators, stationary or nonstationary, one-time or many-time.

The Ito-type stochastic equations

$$\dot{y}_\alpha = f_\alpha(y) + \sum_s \sigma_\alpha^{(s)}(y) \xi^{(s)}(t), \quad (\text{A7.1})$$

where $\xi^{(s)}(t)$ are random functions delta-correlated in time, are understood as the limit of the equations

$$\tau^{-1} [y_\alpha(t + \tau) - y_\alpha(t)] = f_\alpha(y(t)) + \sum_s \sigma_\alpha^{(s)}(y(t)) \tau^{-1} \int_t^{t+\tau} \xi^{(s)}(t') dt' \quad (\text{A7.2})$$

for $\tau \rightarrow 0$. Symbolically, the limit of (A7.2) can be written as

$$\dot{y}_\alpha = f_\alpha(y) + \sum_s [\sigma_\alpha^{(s)}(y)]_{-\mu} \xi^{(s)}(t), \quad (\text{A7.3})$$

where $[\dots]_{-\mu}$ is the shift in time: $[\sigma(y(t))]_{-\mu} = \sigma(y(t - \mu))$, and μ is a small positive quantity. If the delta-correlated processes are approximated by the δ_ε -correlated processes with nonzero correlation time ε , then μ in (A7.3) must be far larger than ε , but far smaller than the relaxation time of the system.

We will suppose that the processes $\xi^{(s)}(t)$ have zero mean and are independent of one another. Then their correlators will be

$$\langle \xi^{(s)}(t) \rangle = 0, \quad \langle \xi^{(s_1)}(t_1), \dots, \xi^{(s_n)}(t_n) \rangle = D_n^{(s_1)} \delta_{s_1 \dots s_n} \delta(t_1, \dots, t_n), \quad (\text{A7.4})$$

where $n \geq 2$, $\delta_{s_1 \dots s_n} = \delta_{s_1 s_2} \dots \delta_{s_1 s_n}$, $\delta(t_1, \dots, t_n) = \delta(t_{12}) \delta(t_{13}) \dots \delta(t_{1n})$. Using (2.3.25), from (A7.2, 4), we can easily compute the coefficient of the master equation

$$K_\alpha(y) = f_\alpha(y), \quad K_{\alpha_1 \dots \alpha_n}(y) = \sum_s D_n^{(s)} \sigma_{\alpha_1}^{(s)}(y) \dots \sigma_{\alpha_n}^{(s)}(y), \quad n \geq 2. \quad (\text{A7.5})$$

If we denote the fluctuational term by $F_\alpha(y, t)$, so that we could write (A7.3) in the form $\dot{y}_\alpha = f_\alpha(t) + F_\alpha(y_{-\mu}, t)$, then the relationships (A7.5) for $n \geq 2$ will be equivalent to

$$\langle F_{\alpha_1}(y, t_1), \dots, F_{\alpha_n}(y, t_n) \rangle_y = \delta(t_1, \dots, t_n) \sum_s D_n^{(s)} \sigma_{\alpha_1}^{(s)}(y) \dots \sigma_{\alpha_n}^{(s)}(y), \quad (\text{A7.6})$$

where $y = \{y_\alpha\}$ are thought of as fixed independent arguments. Note that the number of the functions $\xi^{(s)}(t)$ in (A7.1) is not predetermined. It should be large enough, so that at any fixed $K_{\alpha_1 \dots \alpha_n}(y)$ the equations (A7.5) hold.

A7.2 Symmetrized Stochastic Equations

A drawback of equation (A7.1), treated as an Ito equation, is the fact that it contains expressions of the type $\sigma(y) \xi(t)$, which cannot, in various computations, be transformed by normal rules suitable for smooth functions. This is rather inconvenient. Normal transformation rules can be applied to the stochastic equation

$$\dot{y}_\alpha = g_\alpha(y) + \sum_s g_\alpha^{(s)}(y) \xi(t) \quad (\text{A7.7})$$

written in symmetrized form (S -sense). We then understand this equation as follows: first we write it for the δ_ε -correlated approximation of the processes $\xi^{(s)}(t)$, and then in the resultant equation we pass to the limit $\varepsilon \rightarrow 0$ to arrive at an equation for the exact delta-correlated processes $\xi^{(s)}(t)$.

To work out an expression for $K_{\alpha_1 \dots \alpha_n}(y)$ in terms of the functions $g_\alpha(y)$, $g_\alpha^{(s)}(y)$ that enter into (A7.7), we should first of all compute $y - [y]_{-\mu}$. We will introduce the notation

$$\Delta_\alpha(t) = y_\alpha(t) - y_\alpha^0 \quad (\text{A7.8})$$

[$y_\alpha^0 = y_\alpha(t_0)$]. If then we denote the right-hand side of (A7.7) by $\kappa G(y(t), t)$, where κ is a formal small parameter, then (A7.7) gives

$$\Delta_\alpha(t) = \kappa \int_{t_0}^t G(y(t'), t') dt' = \kappa \int_{t_0}^t dt' \sum_{m=0}^{\infty} \frac{1}{m!} \frac{\partial^m G}{\partial y^m}(y^0, t') [\Delta(t')]^m. \quad (\text{A7.9})$$

Substituting the expansion $\Delta_\alpha(t) = \sum_{i=1}^{\infty} \kappa^i \Delta_\alpha^{(i)}(t)$ and equating the terms of various orders in κ , we will obtain the various approximations,

$$\begin{aligned} \Delta_\alpha^{(1)}(t) &= \int_{t_0}^t dt' G_\alpha(y^0, t'), \quad \Delta_\alpha^{(2)}(t) = \int_{t_0}^t dt' \frac{\partial G_\alpha}{\partial y_\beta}(y^0, t') \Delta_\beta^{(1)}(t'), \\ \Delta_\alpha^{(3)}(t) &= \int_{t_0}^t dt' \frac{\partial G_\alpha}{\partial y_\beta}(y^0, t') \Delta_\beta^{(2)}(t') \\ &\quad + \frac{1}{2} \int_{t_0}^t dt' \frac{\partial^2 G_\alpha}{\partial y_\beta \partial y_\gamma}(y^0, t') \Delta_\beta^{(1)}(t') \Delta_\gamma^{(1)}(t'), \dots . \end{aligned} \quad (\text{A7.10})$$

Using these and taking account of the way in which κG is expressed through $g^{(s)}(y)$ and confining ourselves to $\Delta^{(1)}$ and $\Delta^{(2)}$, we get

$$\begin{aligned} y_\alpha(t) - y_\alpha^0 &\equiv \Delta_\alpha(t) = \sum_s g_\alpha^{(s)}(y^0) \int_{t_0}^t dt' \xi^{(s)}(t') \\ &\quad + \sum_{s,r} \frac{\partial g_\alpha^{(s)}}{\partial y_\beta}(y^0) g_\beta^{(r)}(y^0) \int_{t_0}^t dt' \xi^{(s)}(t') \int_{t_0}^{t'} dt'' \xi^{(r)}(t'') + \dots . \end{aligned} \quad (\text{A7.11})$$

We have here discarded the terms of order $(t - t_0)^2$ and above, which contain $g_\alpha(t)$ and are of no consequence for the final result.

Let us set $t_0 = t - \mu$ in (A7.8) and (A7.11). Then (A7.8, 11) will coincide with $y_\alpha - [y_\alpha]_{-\mu}$. Substituting the expansion

$$g_\alpha^{(s)}(y) = [g_\alpha^{(s)}(y)]_{-\mu} + \left[\frac{\partial g_\alpha^{(s)}(y)}{\partial y_\beta} \right]_{-\mu} \Delta_\beta + \frac{1}{2} \left[\frac{\partial^2 g_\alpha^{(s)}(y)}{\partial y_\beta \partial y_\gamma} \right]_{-\mu} \Delta_\beta \Delta_\gamma + \dots , \quad (\text{A7.12})$$

into (A7.7) and using (A7.11), we will transform (A7.7) to

$$\begin{aligned}
\dot{y}_\alpha &= g_\alpha(y) + \sum_s [g_\alpha^{(s)}(y)]_{-\mu} \xi^{(s)}(t) \\
&\quad + \sum_{s,r} \left(\frac{\partial g_\alpha^{(s)}}{\partial y_\beta} g_\beta^{(r)} \right)_{-\mu} \xi^{(s)}(t) \int_{t-\mu}^t dt' \xi^{(r)}(t') \\
&\quad + \sum_{srq} \left(\frac{\partial g_\alpha^{(s)}}{\partial y_\beta} \frac{\partial g_\beta^{(r)}}{\partial y_\gamma} g_\gamma^{(q)} \right)_{-\mu} \xi^{(s)}(t) \int_{t_0}^t dt' \xi^{(r)}(t') \int_{t_0}^{t'} dt'' \xi^{(q)}(t'') \\
&\quad + \frac{1}{2} \sum_{srq} \left(\frac{\partial^2 g_\alpha^{(s)}}{\partial y_\beta \partial y_\gamma} g_\beta^{(r)} g_\gamma^{(q)} \right)_{-\mu} \xi^{(s)}(t) \int_{t_0}^t dt' \xi^{(r)}(t') \int_{t_0}^t dt'' \xi^{(q)}(t'') + \dots
\end{aligned} \tag{A7.13}$$

As in (A7.3), the values of y on the right-hand side of (A7.13) are taken at earlier times $t - \mu$ than ξ (taken at t); therefore, ξ and y may be considered statistically independent of one another. Using this independence, we can readily find the coefficients $K_{\alpha_1 \dots \alpha_n}$ in any approximation. We then should bear in mind that, because the correlators $\langle \xi^{(s)}(t_1), \dots, \xi^{(s)}(t_n) \rangle$ are symmetrical in t_1, \dots, t_n [see (A7.4)] both for the exact and approximate delta function, we have

$$\int_{t_1 > t_2 > \dots > t_n} \delta(t_1, t_2, \dots, t_n) dt_2 \dots dt_n = (n!)^{-1} \tag{A7.14}$$

The analogous integral of $\langle \xi^{(s)}(t_1), \dots, \xi^{(s)}(t_n) \rangle$ is equal to $D_n^{(s)}/n!$. Considering the terms written explicitly in (A7.13), we obtain with the help of (2.3.25)

$$\begin{aligned}
K_\alpha(y) &= g_\alpha(y) + \frac{1}{2} \sum_s \frac{\partial g_\alpha^{(s)}(y)}{\partial y_\beta} g_\beta^{(s)}(y) \\
&\quad + \frac{1}{6} \sum_s \left(\frac{\partial g_\alpha^{(s)}}{\partial y_\beta} \frac{\partial g_\beta^{(s)}}{\partial y_\gamma} g_\gamma^{(s)} + \frac{\partial^2 g_\alpha^{(s)}}{\partial y_\beta \partial y_\gamma} g_\beta^{(s)} g_\gamma^{(s)} \right) + O(K_{\beta\gamma\sigma\rho}), \\
K_{\alpha\beta}(y) &= \sum_s g_\alpha^{(s)}(y) g_\beta^{(s)}(y) \\
&\quad + \frac{1}{2} \sum_s \left(\frac{\partial g_\alpha^{(s)}}{\partial y_\gamma} g_\beta^{(s)} + g_\alpha^{(s)} \frac{\partial g_\beta^{(s)}}{\partial y_\gamma} \right) g_\gamma^{(s)} + O(K_{\beta\gamma\sigma\rho}), \\
K_{\alpha\beta\gamma}(y) &= \sum_s g_\alpha^{(s)}(y) g_\beta^{(s)}(y) g_\gamma^{(s)}(y) + O(K_{\beta\gamma\sigma\rho}).
\end{aligned} \tag{A7.15}$$

More accurate equations are also possible.

In comparison to (A7.5), expressions (A7.15) contain some additional terms. If $K_{\alpha_1 \dots \alpha_n}(y)$ are small and decrease monotonically with n , as is the case with intrinsic noise in physical systems (when $K_{\alpha_1 \dots \alpha_n}(y) \sim (kT)^{n-1}$ and analogously for shot noise), the above-mentioned corrections are small. In a first approximation they may be ignored, i.e. we need make no distinction between the two senses in which the stochastic equations are understood. A more rigorous treatment must take into account this difference.

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Izv. VUZ Radiofizika	Sov. Radiophysics
Teor. Mat. Fiz.	Sov. Phys. – Theor. Math. Phys.
Zh. Eksp. Teor. Fiz.	Sov. Phys. – JETP

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