# METHODOLOGICAL NOTES

# Fluctuation-dissipation relations. Achievements and misunderstandings

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<u>Abstract.</u> We discuss the 'generalized fluctuation-dissipation relations (theorems)' introduced for the first time in our work of 1977–1984 as statistical-thermodynamic consequences of time symmetry (reversibility) of microscopic dynamics. We show, in particular, that various similar relations, including 'fluctuation theorems' that have appeared since the 1990s, are, in essence, alternative formulations or special cases of our old results.

# 1. Introduction

Interest in rigorous theoretical results of nonequilibrium statistical physics reflecting the fundamental properties of microscopic motion has been growing explosively during the last fifteen years. One of reasons for this interest is the discovery of new possibilities of experimental justification of the theory on the mesoscopic level. Several important experiments and aspects of the underlying theory were recently reviewed in *Physics–Uspekhi* by Pitaevskii [1]. However, because of its brevity, that paper did not cover

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Received 1 August 2012, revised 23 April 2013 Uspekhi Fizicheskikh Nauk **183** (6) 617–630 (2013) DOI: 10.3367/UFNr.0183.201306d.0617 Translated by authors; edited by A M Semikhatov some other aspects of the subject, in particular, those appearing in the current literature and involving significant misunderstandings. In this paper, we highlight all that, too.

To point out immediately what we have in mind, we start with the example considered in [1].

### 1.1 Jarzynski and Crooks relations

Any use of the presently popular Jarzynski [2, 3] and Crooks [4-6] equalities or relations - excellently expounded in [1]presumes that a physical system under consideration has a definite thermodynamically equilibrium state at an arbitrary constant value, x = const, of a parameter x of its Hamiltonian. For instance, a torsion pendulum in a liquid [1] finds a definite equilibrium position (with equilibrium fluctuations around it) at any constant value of the torque x. Any given x = const then determines a value F(x) of the free energy of the system as a characteristic of its corresponding equilibrium state, and we can therefore speak about changes in the free energy,  $\Delta F$ . For example, when the initial equilibrium of the system at t = 0 is perturbed by some variations of its parameter x(t), the Jarzynski and Crooks (JC) equalities relate the system energy fluctuations in this process to the quantity  $\Delta F = F(x(t)) - F(x(0))$ .

# 1.2 Peculiarities of open systems

We now assume that the pendulum arm is made movable (inserted into a bearing), such that the pendulum becomes a rotor. The resulting system—an analogue of the rotary viscosimeter—can stay in equilibrium at the zero value of the torque only, x = 0. If  $x \neq 0$ , this system is driven to a nonequilibrium (dissipative) state, where the rotor is constantly rotating. In such a state, the system free energy has no

definite value, merely because it has no general theoretical definition for thermodynamically nonequilibrium systems. Consequently, its changes  $\Delta F$  are not defined, either.

Similarly, a conducting medium can stay in equilibrium only at a zero value of its Hamiltonian parameter such as the electric field, and the aforesaid also concerns this system. Here, we call such systems 'open', while their opposite is 'closed'.

It follows from the above discussion that the JC equalities can be applied to open systems at exceptional time instants only, when the condition of a 'cyclic process' (the term from [7]; see Section 1.4) is satisfied: x(t) = x(0) = 0. This fact makes the JC equalities practically fruitless for nonequilibrium states (see Sections 2.7 and 2.9).

## 1.3 Old (fluctuation-dissipation) relations

Exact relations applicable to open systems without any additional conditions were obtained more than thirty years ago in our work [8–15]. They are valid at every time instant regardless of current values of the parameters, and therefore constantly produce information about a nonequilibrium state. Obviously, objects such as the free energy changes  $\Delta F$  cannot appear in these relations in principle. Therefore, it is sufficient for the use of the relations that an equilibrium state exist at least at one point (x = 0). Hence, they also extend to closed systems, to which the JC equalities in fact pertain.

This advantage of our relations is that they deal with fluctuations of not the full energy of a system but the part without the energy of interaction with the environment (responsible for the parameters), that is, internal energy, which is more closely related to dissipation.

#### 1.4 Misunderstandings

The aforesaid explains why the opinion common in the literature (see, e.g., review article [16] and the related references in [17]) that our relations are particular cases of the JC relations (or that the latter 'reduce' to ours in particular cases) is a misunderstanding.

The origin of such misunderstandings can be seen from Jarzynski's article [7], where the author compares the old (our) and the new (JC) relations and concludes that they are equivalent in the special case of 'cyclic processes'.<sup>1</sup> We can agree with this statement, but in a purely formal sense only and only for closed systems, because it was assumed in [7] that systems under consideration have equilibrium states at any values of their parameters. In other words, the existence of open systems was not taken into account in [7]. Hence, the comparison made was superficial, based on the appearance of  $\Delta F$  (see above), which is an important component of the new (JC) relations but is absent in the old ones (ours). From the standpoint of [7], this difference looks like a defect in our theory, which is eliminated in the case of 'cyclic processes' only,<sup>2</sup> when  $\Delta F = 0$  in the JC theory. For these reasons, it is not surprising that the formally neutral conclusion in [7] is interpreted by the readers of that paper as an indication of the particular character of our results.

More precisely, there are papers [18, 19] free of such interpretations, but qualitative differences between the two types of systems are not accentuated there, either. Therefore, the subject does require a discussion.

We do not pretend to review generalized fluctuationdissipation relations — as we think of the subject — but hope that the following notes will be useful for interested readers. For simplicity and brevity, we confine our consideration to classical mechanics, following our remarks in [17] and short review [1] (it strongly motivated us, for which we are grateful to its author).

# 1.5 History of the subject

Preliminarily, we recall that the interest in rigorous results of statistical mechanics has a very long history. They include the Kirchhoff law [20], the Einstein relation [21, 22], the Nyquist formula [23, 24], and the unifying fluctuation–dissipation theorem (FDT) [20, 25]. Later, Efremov's 'quadratic FDT' [26, 27], Stratonovich's 'four-index relations' [28, 29], and his Markovian nonlinear fluctuation–dissipation theory [29, 30] appeared. In 1977–1981, we first obtained [8] and investigated [9–13] the 'generalized fluctuation–dissipation relations' (FDRs), or theorems [11, 12], in a universal way, connecting probabilities of observation of mutually time-reversed processes and changes in the system entropy during these processes. The first such relation was formula (7) in [8], and the most general of them is equality (2) in [31]:

$$P(\Pi_{+})\exp\left(-\Delta S(\Pi_{+})\right) = P(\Pi_{-}), \qquad (1)$$

where the symbol  $\Pi_+$  denotes some process, i.e., a collection of results of observations and measurements of some sorts that can be realized in a given system under given conditions (concerning the initial state and external perturbations of the system),  $\Pi_{-}$  is the time reversal of  $\Pi_{+}$  (in this respect, the reversion applies to both the results and conditions),  $P(\Pi_{\pm})$  are the probabilities of the realization of these processes (to be precise, the results of measurements), and  $\Delta S(\Pi_{+}) = -\Delta S(\Pi_{-})$  is the system entropy change in the forward process. This formula covers both closed and open systems, and extends to processes that not only finish in but also start from thermodynamically nonequilibrium states (see Section 3.2). In the same studies and in [15, 32–36], we (and later one of us in [37-42]) considered other forms of FDRs (first of all, in terms of characteristic functionals) and their various consequences and applications.

We note that formula (1), published in 1984 as a summary of our results, exceeds analogous relations, including 'fluctuation theorems' [16, 18, 19, 43] published in 1997 and later by Jarzynski, Crooks, and their followers. This statement does not reduce the importance of Jarzynski's and Crooks's work, which introduced new theoretically attractive and practically useful forms of FDRs (see Sections 2.2, 2.4, 3.2, 3.3) and initiated the current 'boom' in this field.

# 2. Statistical equalities for nonequilibrium processes

# 2.1 Hamiltonians, their parameters,

# and two types of systems

We speak about Hamiltonian dynamical systems under external influences. Such systems are described by parameters x of their Hamiltonians,  $H(q, p, x) = H(\Gamma, x)$ ,

<sup>&</sup>lt;sup>1</sup> "For the special case of *cyclic* processes, in which the perturbation is turned on and then off, Eqns (1) and (2) are equivalent" [7], p. 496. Here, equalities (10) and (12) are meant. We compare them from our standpoint in Sections 2.7, 2.9, and 3.3–3.5.

 $<sup>^2</sup>$  In fact, we never imposed 'cyclic' or any other restrictions on time variations of parameters. This can be easily verified as regards our main works [8–10], which are easily accessible through the Internet.

where  $\Gamma = \{q, p\}$  are canonical microscopic variables. The parameters can vary with time in accordance with a given law. The  $\Gamma$  values at an arbitrary instant,  $\Gamma(t)$ , are in a definite oneto-one correspondence, determined by the Hamilton equations of motion, with values at any other instant, for instance,  $\Gamma(0) \equiv \Gamma$ . According to the Hamilton equations, the system total energy  $H(t) = H(\Gamma(t), x(t))$  changes only if the parameters change, such that

$$\frac{\mathrm{d}H(t)}{\mathrm{d}t} = \frac{\mathrm{d}x(t)}{\mathrm{d}t} \frac{\partial H(\Gamma(t), x(t))}{\partial x(t)} = -\frac{\mathrm{d}x(t)}{\mathrm{d}t} Q(t), \qquad (2)$$

where  $Q(t) = Q(\Gamma(t), x(t))$  and  $Q(\Gamma, x) = -\partial H(\Gamma, x)/\partial x$  are the system internal variables conjugate to the parameters.

If the system is closed, changes in its total energy H(t) quite reasonably characterize changes in the system state, as is the case with the JC relations. The openness of a system, in the sense outlined in the Introduction, presumes that at  $x \neq 0$  it may accept an unboundedly large amount of energy from its environment (sources of external influences) even if the parameters x are kept constant, x = const. However, according to (2), the total energy H(t) also stays constant. This means that changes in one of its parts—its internal, or intrinsic, energy—are compensated by changes in another part, the energy of the system interaction with the environment. Thus, H(t) is no longer a proper characteristic of the system state, and it is more meaningful to deal instead with the system internal energy  $H_0(t)$ .

A typical interconnection between H(t) and  $H_0(t)$  can be illustrated with the examples of a torsion pendulum and rotor in Section 1.2. Evidently, for both of them, the rate of change of the internal energy  $H_0(t)$  is nothing but the work produced by the torque x(t) per unit time,

$$\frac{\mathrm{d}H_0(t)}{\mathrm{d}t} = x(t) \frac{\mathrm{d}Q(t)}{\mathrm{d}t},\tag{3}$$

where Q(t) means the rotation angle. At the same time, the rate of change of H(t) is expressed by (2), with Q(t) being the same rotation angle (see formulas (5) and (25) in [1]). After subtracting (3) from (2), it follows that the interaction energy  $H - H_0$  satisfies the equation  $d(H - H_0)/dt = -d(xQ)/dt$ , and hence  $H(t) - H_0(t) = -x(t)Q(t)$  up to a constant.

It is natural to supplement this with the assumption that  $H_0(t) = H_0(\Gamma(t))$ , that is, the internal energy has no explicit dependence on x. Then, from the arbitrariness of the function x(t) and of the phase trajectory  $\Gamma(t)$ , it follows for both systems that

$$H(\Gamma, x) = H_0(\Gamma', Q) - xQ = H_0(\Gamma) - xQ(\Gamma), \qquad (4)$$

where  $Q(\Gamma)$  also has no explicit dependence on x. Here, after the first equality sign, the angle Q is considered an independent (canonical) variable, and  $\Gamma'$  denotes all the other variables. In the expression after the second equality sign, it is assumed that Q can in general be a function of a different canonical set of variables [then  $Q(t) = Q(\Gamma(t))$ ]. Hamiltonians of form (4) can be termed 'bilinear' because the interaction with the environment is there linear separately in the parameters x and the conjugate internal variables Q.

Clearly, a difference between a pendulum and a rotor is that the rotor can make an arbitrary number of full turns, that is, its angle Q(t) can vary over an infinite range. In (4),

this difference is invisible<sup>3</sup> because it is hidden in the system eigen-Hamiltonian  $H_0(\Gamma', Q)$ . It can either include (for a pendulum) or not include (for a rotor) an elastic contribution unboundedly increasing as Q increases, for instance,  $cQ^2/2$  (if the elasticity of the pendulum wire or ribbon obeys Hooke's law). If it is absent (in the case of a rotor), then  $H_0(\Gamma', Q \pm 2\pi) = H_0(\Gamma', Q)$ ; therefore, arbitrarily large translations of Q can change the Hamiltonian by an immaterial constant only.

It is obvious that all open systems (OSs) interact with their environment via such variables, indifferent to shifts, and therefore Hamiltonians of OSs are naturally bilinear.

We consider differences between OSs and closed systems (CSs) from the standpoint of statistical mechanics, where the use of the probability distribution of microscopic states of the system  $D(q,p;t) = D(\Gamma;t)$  is indispensable. Following the principles of the Gibbs statistical mechanics, we have to represent thermodynamical equilibriums of systems with constant parameters by the classical canonical distributions

$$D_{\rm eq}(\Gamma, x) = \exp\left(\frac{F(x) - H(\Gamma, x)}{T}\right),\tag{5}$$

where *T* is the system temperature (in energy units) and *F*(*x*) is the abovementioned free energy, to be determined from the probability normalization condition  $\int D(\Gamma; t) d\Gamma = 1$ .

In the case of a torsion pendulum, for instance, with the Hooke elasticity, it follows from (4) and (5) that  $\Delta F = F(x) - F(0) = -x^2/2c$  (formula (26) in [1]). For a rotor, Hamiltonian (4) becomes a linear function of Q, and the integral along the Q axis in (5) diverges. At x = 0, the divergence is linear; therefore, distribution (5) has the probability-theoretical meaning of the limit of a uniform distribution along Q. But if  $x \neq 0$ , then the divergence is exponential and expression (5) no longer allows a reasonable probabilistic interpretation. In other words, at  $x \neq 0$ , such a system has no equilibrium states, and there are no grounds to speak about its free energy.

# 2.2 Two types of parameters and the relations of 'old' and 'new' results

Of course, not all applications are amenable to simple bilinear Hamiltonians like (4), first of all, if we are talking about CS or 'mixed' systems that are open with respect to some of their parameters but closed with respect to others. However, any Hamiltonian that is a sufficiently 'good' function of its arguments can be written in the form

$$H(\Gamma, x) = H_0(\Gamma) - h(\Gamma, x), \qquad (6)$$

with the condition  $h(\Gamma, 0) = 0$  ensuring the uniqueness of this decomposition. The origin x = 0 in the parameter space of a CS can be defined in any suitable way, e.g., as a point of an extremum of the free energy, where  $\partial F(x)/\partial x = 0$ , thus corresponding to an 'unperturbed system'.

It is just for such Hamiltonians that the main results in our work [8, 11,12] were deduced, as was clearly pointed out there; for a better visualization of the formulas, however, most of them were displayed in terms of bilinear Hamiltonians.<sup>4</sup> Anyway, form (4) or (6) includes systems with

<sup>&</sup>lt;sup>3</sup> Nevertheless, already in 1977, interest in open systems was so great that explanations of their existence seemed unnecessary at that time.

<sup>&</sup>lt;sup>4</sup> But we note that any 'good' Hamiltonian can be represented in bilinear form (4) if x is a proper set of effective parameters (functions of actual parameters) and xQ is their contraction ('scalar product') with a corresponding set of phase functions.

parameters of the abovementioned type, which can be named 'force parameters' (FPs), or 'forces', because they frequently represent forces in the sense of physical mechanics, or their potentials, or fields (or their sources if the fields themselves are a constituent part of a system).

Some additions can be required if decomposing the Hamiltonian as in (6) becomes unnecessary because  $H(\Gamma, x)$  itself already represents the system internal energy, or even impossible because  $H(\Gamma, x)$  is too singular a function of some of its arguments.

One example is where x is the position of a movable edge of a spring immersed in a liquid (thermostat). In experiments with ribonucleic acids (RNA), well described in [1], the role of the spring is played by a pack of RNA molecules. In this system,  $Q = -\partial H/\partial x$  acquires the meaning of the force acting from the spring on a transmitter of external influence ('actuator'), and hence (2) is just the external work (per unit time) against the system.

Another example is given by wine in wineskins, whose position and deformations serve as parameters of the system. The singularity of the Hamiltonian (and especially the Poisson brackets) here, as well as in the previous example, occurs because changes in the Hamiltonian parameters simultaneously change its domain in the phase space.

Parameters of this type, which determine the positions of some elements or boundaries of a system, can be named 'positional parameters' (PPs). They must change in a continuous way, because their instant change would mean infinitely fast displacements of some parts of the system. A decomposition like (6) would be incorrect for such parameters because the domains of  $H(\Gamma, x \neq 0)$  and  $H(\Gamma, 0) = H_0(\Gamma)$  are different.

By contrast, 'force parameters' do not have to be varying continuously and can in principle make instant jumps because such jumps do not change the current microscopic state of a system; instead, they merely redirect its further evolution. For example, the force parameter (torque) of a torsion pendulum can be 'switched' instantly in theory and practically instantly in experiment, due to the possibility of a fast enough operation with the electric current (in a magnetic field) that creates the torque (see [1, 44]).

The parameters of OSs certainly belong to this 'force' type. Indeed, if any deviation of a parameter from zero drives the system into constant motion, then the rate of the deviations is not essential for its behavior.

From all the aforesaid, it follows that neither the first new (JC) results (from 1997–1999) nor our (BK) first old results (from 1977–1979) are quite 'all-embracing', and their relations to reality can be reflected by Table 1.

However, our slightly later relation (1) also fully covers the last column of Table 1, as well as FDRs (2.25) and (2.26)

Table 1. Applicable areas  $^{\ast}$  of the results of Jarzynski–Crooks (JC) and Bochkov–Kuzovlev (BK).

Authors	Publication	Open systems	Closed systems		
	years		FP**	PP ***	
JC BK	1997 – 1999 1977 – 1979	Yes	Yes Yes	Yes —	
* 'Yes' in a cell means the applicability in general; the dash means applicability under special conditions only. ** Force parameters.					

\*\*\* Positional parameters.

in [11], which were intended for CSs and are completely transferable to the case of PPs because, in fact, they do not resort to decomposition (6). On the other hand, today's followers of Jarzynski and Crooks move to the OS column in Table 1.

### 2.3 Liouville theorem and statistical equalities

We now compare the 'new' and 'old' relations. All of them wholly or substantially result from the Liouville theorem [45] saying that the Jacobian of a canonical variable transformation from  $\Gamma = \Gamma(0)$  to  $\Gamma(t)$  is always equal to unity,  $d\Gamma/d\Gamma(t) = 1$  (the phase volume is conserved).

It is convenient to first derive one trivial but significant statistical identity. Let  $D_1(\Gamma)$  and  $D_2(\Gamma)$  be two probability distributions, both normalized to unity and nowhere vanishing. We first note that because of the Liouville theorem,  $\int D_2(\Gamma(t)) d\Gamma = \int D_2(\Gamma(t)) d\Gamma(t) = 1$ . Second, dividing and multiplying the integrand here by  $D_1(\Gamma)$ , we have

$$\int \exp\left(\ln \frac{D_2(\Gamma(t))}{D_1(\Gamma)}\right) D_1(\Gamma) \,\mathrm{d}\Gamma = 1\,. \tag{7}$$

Third, replacing  $D_1$  and  $D_2$  here with two canonical distributions (5),  $D_1(\Gamma) = D_{eq}(\Gamma, a)$  and  $D_2(\Gamma) = D_{eq}(\Gamma, b)$  with some *a* and *b*, we obtain the equality

$$\exp\left(\frac{F(b) - F(a)}{T}\right) \left\langle \exp\left(-\frac{H(\Gamma(t), b) - H(\Gamma, a)}{T}\right) \right\rangle_{a} = 1,$$
(8)

where the angular brackets denote averaging over the canonical distribution of the initial conditions  $\Gamma = \Gamma(0)$  of the phase trajectory  $\Gamma(t)$ :

$$\langle \ldots \rangle_x = \int \ldots D_{\text{eq}}(\Gamma, x) \,\mathrm{d}\Gamma,$$
 (9)

with the subscript indicating the parameters of the initial distribution.

Identities like (8) or (25) in Section 3.2 below are satisfied regardless of the magnitudes and rates of time variations of the parameters and the degree of nonequilibrium induced by them; therefore, such identities indicate the existence of universal relations (just what we call 'FDRs') between the characteristic (average or most probable) direction of the system evolution and the accompanying nonequilibrium fluctuations.

#### 2.4 Jarzynski equality

We set a = x(0) and b = x(t) in identity (8). It then turns into the 'Jarzynski equality' (JE) [1, 2]:

$$\exp\left(\frac{\Delta F(t)}{T}\right) \left\langle \exp\left(-\frac{W(t)}{T}\right) \right\rangle_{x(0)} = 1, \qquad (10)$$

where  $\Delta F(t) = F(x(t)) - F(x(0))$  and W(t) is the change of the system total energy during the observation time. According to (2),

$$W(t) = H(\Gamma(t), x(t)) - H(\Gamma, x(0)) = -\int_0^t \frac{\mathrm{d}x(t')}{\mathrm{d}t'} Q(t') \,\mathrm{d}t',$$
(11)

with  $Q(t) = Q(\Gamma(t), x(t))$  and  $Q(\Gamma, x) = -\partial H(\Gamma, x)/\partial x = \partial h(\Gamma, x)/\partial x$ .

The Jarzynski equality is applicable to any CS, including the case of a PP (see Section 2.2). But for OSs, it makes sense only if x(0) = 0 and, in addition, also x(t) = 0 at the current instant (i.e., external influences disappear), because in the case of an OS with  $x(0) = a \neq 0$ , the canonical initial distribution required in (8) does not exist, and with  $x(t) = b \neq 0$ , the required free energy F(b) is not defined. At x(t) = x(0) = 0, when the JE is meaningful, it coincides with our equality (12).

# 2.5 Bochkov-Kuzovlev equality

We now set a = b = 0 in (8). In the case of an OS, as we already know, this is the only allowable choice. Then identity (8) implies

$$\left\langle \exp\left(-\frac{E(t)}{T}\right)\right\rangle_{0} = 1,$$
 (12)

where  $E(t) = H_0(\Gamma(t)) - H_0(\Gamma)$  is a change in the internal, or intrinsic, energy of the system during its observation. By the Hamiltonian equations of motion,

$$E(t) = \int_0^t \frac{\mathrm{d}\Gamma(t')}{\mathrm{d}t'} \frac{\partial h\big(\Gamma(t'), x(t')\big)}{\partial \Gamma(t')} \,\mathrm{d}t' \,. \tag{13}$$

If the Hamiltonian is bilinear, Eqn (4), this expression is simplified, in accordance with (3), to

$$E(t) = \int_0^t x(t') \frac{dQ(t')}{dt'} dt'.$$
 (14)

Here,  $x(0) \neq 0$  in general, that is, external forces are not assumed to be absent at the beginning of observation.

Equality (12) appeared for the first time in [8] from more general relations that involved a time-reversed evolution (see Section 3). Evidently, just this equality was mentioned in [1] as the 'Bochkov–Kuzovlev equality' (BKE).

In contrast to the JE, the BKE is freely applicable to OSs at any instant, independently of the current values of parameters x(t), and to steady nonequilibrium (dissipative) states. As regards CSs, the BKE is freely applicable to them in the case of FPs, but in the case of PPs under special conditions only, x(t) = x(0) = 0 [because otherwise the domain of  $\Gamma(t)$  in (8) would be different from that of  $\Gamma(0)$ , and the latter would differ from the domain of  $H_0(\Gamma)$ ]. Then the BKE coincides with the JE.

### 2.6 Physical interpretation

## of statistical equalities and jumps of external forces

The subscript x(0) at the angular brackets in JE (10) emphasizes that the parameters of the initial (at t = 0) canonical distribution of microstates of a system coincide with parameters of its Hamiltonian at the initial instant. Usually, this goes without saying, and it is thought that the JE applies to a system that before t = 0 was in equilibrium, with constant parameters equal to x(0).

But, in fact, the parameters of the initial distribution in no way affect the behavior of one concrete phase trajectory or another, either before or after t = 0. Therefore, first, the inequality  $x(0) \neq a$  in (8) is possible and by itself does not say that at t = 0 there is a jump of Hamiltonian parameters from a to x(0). Second, the system equilibrium before t = 0 is an additional independent assumption not implied automatically by the subscript. Without it, just the same canonical distribution can appear in theory in the role of model characteristics of nonequilibrium states (see Section 2.10).

On the other hand, testing the JE or BKE experimentally (see Section 2.8) indeed requires practical realization of the mentioned additional condition, that is, the relaxation to equilibrium, or 'thermalization', of the system (at t < 0) being governed by a Hamiltonian with parameters equal to *a* [otherwise, it would be unrealistic to organize a sampling of experiments properly corresponding to  $D_{eq}(\Gamma, a)$ ]. Then, jumps  $x(0) \neq a$  acquire a literal sense. But as we underlined in Section 2.2, this is quite rightful behavior of FPs, because their jumps do not destroy the continuity of the time evolution of (canonical) microscopic variables.

For these reasons, cases of discontinuities, or jumps, of the force parameters (FPs)—such as  $x(0) \neq a$  in (8) or  $x(0) \neq 0$  in (12)—are no less important for the theory and its applications<sup>5</sup> than the case x(0) = a assumed in the JE. Here, a quantum mechanical analogy is relevant as follows: when considering the evolution of a system with a timedependent Hamiltonian H(t), it would be absurd in general to confine consideration to the initial system states (at t = 0) that are eigenstates of H(0) or to the initial density matrix that commutes with H(0). If, nevertheless, jumps of FPs seem unrealistic in some application of the theory, then this indicates the necessity of revising the system model, but not depriving the FPs of their natural rights. Indeed, in any physically correct model, characteristic temporal scales of the system response to external perturbations must be determined by the system itself, not by outside 'censorship'. Hence, abandoning the FP jumps would be as senseless as abandoning the Heaviside step function or Green's functions and other useful idealizations.

We note in addition that in the case of PPs, the same can be said about their time derivatives dx(t)/dt, which can also make jumps [that is, x(t) can be piecewise continuous linear functions of time].

# 2.7 Comparison between JE and BKE

According to Sections 2.4 and 2.5, it remains only to consider the CS–FP case. We do this at x(0) = 0, where the JE and BKE apply to the same statistical ensemble, the one defined by the initial distribution  $D_{eq}(\Gamma, 0)$ . We then merely have to compare the random (fluctuating) quantities W(t) and E(t) in the exponents in (10) and (12). Forming their difference, from (11) and (13) or (14), we have

$$W(t) - E(t) = h(\Gamma, x(0)) - h(\Gamma(t), x(t))$$
  
= x(0) Q(0) - x(t) Q(t), (15)

with the last expression corresponding to bilinear Hamiltonians. Hence, with x(0) = 0, we can rewrite BKE (12) in a form convenient for comparison:

$$\left\langle \exp\left(-\frac{W(t)+x(t)Q(t)}{T}\right)\right\rangle_{0} = 1,$$
 (16)

<sup>5</sup> A variation of jump-like (piecewise constant) dependences x(t), along with variational differentiation in respect to x(t), helps transform generalized FDRs (statistical equalities) like (1) or (12) into various relations between linear and nonlinear response functions (Green's functions, susceptibilities, conductances, etc.) and irreducible second-, third-, and higher-order statistical correlations (cumulants) of fluctuations (see [8, 9, 31, 34–38] for the examples).

where the random term -x(t)Q(t) replaces the nonrandom F(x(t)) - F(0).

Thus, JEs and BKEs deal with essentially different random quantities (functionals of the system history) and therefore mutually supplement one another. Differences between them disappear at the special instants when x(t) = x(0) = 0. But, obviously, it would then be wrong to say that one of the two equalities 'reduces' to the other.

Moreover, the statement that the JE and the BKE are 'equivalent' for 'cyclic processes' [7] (see Section 1.4) is not quite correct either. This can be seen from the following thought experiment. We assume that a parameter — for instance, the pendulum torque-smoothly changes from x(0) = 0 to  $x(t_0) = x_0 \neq 0$  and then rapidly (during a time  $\delta t$  much shorter than characteristic time scales of the pendulum motion) returns to the initial value:  $x(t_0 + \delta t) = 0$ . It is clear from (14) that the quantity E barely changes during this return:  $E(t_0 + \delta t) - E(t_0) \propto \delta t$ . Simultaneously, according to (11) and (15), the quantity W achieves the coincidence  $W(t_0 + \delta t) = E(t_0 + \delta t)$  by means of the jump  $W(t_0 + \delta t) - W(t_0) \approx x_0 Q(t_0)$  practically independent of  $\delta t$ . We can therefore say that in essence the coincidence of W and E after 'cycling' of the process is nothing but an artifact having no relation to the actual physical contents of these quantities.

It is also useful to consider two more special experiments. Let the torque increase from x(0) = 0 so slowly (the observation time be so long) that the process can be considered adiabatic. Then W(t) in JE (10) is almost (asymptotically) free of fluctuations and merely reduces to the constant  $\Delta F(t)$ . Accordingly, BKE (16) becomes

$$\exp\left(-\frac{\Delta F(t)}{T}\right) \left\langle \exp\left(-\frac{x(t)Q(t)}{T}\right) \right\rangle_{\text{adiabatic}} = 1,$$

which attests to the fact that fluctuations are quasi-equilibrium in such a process, i.e.,  $D(\Gamma; t) \approx D_{eq}(\Gamma, x(t))$ .

Now, by contrast, let the torque sharply switch on at the very beginning of the observation and later stay constant: x(t > 0) = x = const. Then W(t > 0) = -xQ(0) = const, where  $Q(0) = Q(\Gamma(0))$  obeys the probability distribution  $D_{\text{eq}}(\Gamma, 0)$ . Therefore, the JE degenerates into the bare F(x) definition, thus giving no information about actual changes in the system at t > 0. At the same time, the BKE gives

$$\left\langle \exp\left(-\frac{x(\mathcal{Q}(t)-\mathcal{Q}(0))}{T}\right)\right\rangle_{\uparrow x} = 1.$$
 (17)

Here, the arrows symbolically represent the assumed time dependence of the parameter. This is a nontrivial equality, because its power expansion (or differentiation) with respect to x leads to the 'Green–Kubo formulas' and, moreover, if the elasticity of the pendulum wire (or ribbon) is not of the Hooke type, or the viscosity of the liquid is 'non-Newtonian', and fluctuations are non-Gaussian, to additional 'nonlinear' relations between fluctuations and dissipation. We thus see that general differences between BKEs and JEs are much more interesting than special cases of their 'equivalence'.

### 2.8 Experimental tests of exact results of the theory

If the authors of experiments described in [44] (also see [1]) had known about our old results, they would have been able to test some of them, including BKE (12), along with JE (10) and the Crooks equalities (we have to emphasize once again

that for CS–FP, old and new equalities are valid simultaneously and independently of one another at any values of parameters), or to test equality (16) equivalent to the BKE in application to a torsion pendulum. From (16), it is clear that this does not even need additional measurements. Especially simple for testing is the particular case (17) of jump-like (steplike) torque switching on, which does not even require integrating the measured data.

The same can be said about relations between probabilities of mutually time-reversed processes (see Section 3). In parallel with the Crooks equality [1, 4, 5], with the help of a torsion pendulum, we can also test the relation

$$P(E;x)\exp\left(-\frac{E}{T}\right) = P(-E;\tilde{x}), \qquad (18)$$

where P(E;x) is the probability density distribution of E = E(t) for a given parameter trajectory  $x = x(\tau)$ ( $0 < \tau < t$ ),  $\tilde{x}(\tau) = \epsilon x(t - \tau)$  ( $\epsilon = \pm 1$ ), and initial microstates on both sides are described [as in (12), (16), and (17)] by the distribution  $D_{eq}(\Gamma, 0)$ .

This relation is a direct consequence of the abovementioned formula (7) in [8] or other FDRs for probability functionals (see Sections 3.2–3.4). In the example of a pendulum,  $\epsilon = 1$  and, using the notation in [1], x = M,  $Q = \Theta$ , and  $E(t) = \int_0^t M(t') d\Theta(t')$ , where *M* and  $\Theta$  are the torque and rotation angle.

We consider two particular cases. In the first, the torque switches on by a jump, and is then constant, as at the end of Section 2.7. Thus, equality (18) can be written similarly to (17):

$$P(E;\uparrow \overrightarrow{M}) \exp\left(-\frac{E}{T}\right) = P(-E;\uparrow \overrightarrow{M}), \qquad (19)$$

where *E* is merely  $E(t) = (\Theta(t) - \Theta(0))M$ . We note that in this case, both the forward and reversed processes begin from the zero torque, that is, they are identical in the statistical sense. Nevertheless, both processes are 'noncyclic' because *t* represents an arbitrary time slice. But if the instant *t* is fixed beforehand, then we can make the processes formally 'cyclic' by replacing  $\uparrow \overrightarrow{M}$  with  $\uparrow \overrightarrow{M} \downarrow$ , all the more so because such a replacement does not affect E(t) (see Section 2.7).

In the second case, we let the torque grow with time linearly. Then, in an analogous symbolic notation, formula (18) yields

$$P(E; \nearrow) \exp\left(-\frac{E}{T}\right) = P(-E; \uparrow \searrow), \qquad (20)$$

where forward and reverse processes are now nonidentical. Here, the reversed process begins with a jump and looks cyclic, while the forward one is not [although, again, it can be made cyclic, by a jump back to zero, because E(t) is indifferent to this operation and hence  $P(E; \nearrow) = P(E; \nearrow)$ ]. Possibly, this is an interesting scenario for experimental testing.

Anyway, we note that the practical verification of principles and the exact results of statistical mechanics are at the same time the verification of the validity of one model of the system under consideration or another. For example, the mechanical external excitation of a torsion pendulum is performed with the help of an electric current that flows inside it and a magnetic field that pierces all the system. Therefore, interpreting experiments in terms of the torque and the rotation angle only means the implicit assumption that all possible collateral effects of the current and the field are either weak enough or statistically independent of the observed mechanical motion of the pendulum. More precisely, their disregarded addition E'(t) to E(t), calculated from measurements of the torque and angle, is statistically noncorrelated with E(t), whence  $\langle \exp[-(E+E')/T] \rangle =$  $\langle \exp(-E/T) \rangle \langle \exp(-E'/T) \rangle$  and  $\langle \exp(-E'/T) \rangle = 1$ . Similarly, a description of the experiments with RNA has invoked a Hamiltonian with a PP, namely, the position of a movable 'bead' (see [1]), although factually the system is governed by FPs, such as a voltage drop in a piezoelectric actuator. Again, either the weakness or the statistical independence of collateral channels of an actuator-mediated external perturbation of the system is assumed.

The 'independence' in these examples is nothing but the hypothesis that the microscopic phase volume is conserved separately in different channels (those considered or ignored) of the system interaction with its environment. In reality, of course, this may be a quite wrong assumption for nonequilibrium processes (see, e.g., [31]).

# 2.9 BKE for open systems, or when the JE does not work

After a transition from a CS to an OS, for example, from a torsion pendulum to a rotor, for the reasons expounded in Sections 1.2, 2.1, and 2.4, the JE generally loses its meaning. The difference between W(t) in (11) in the JE and E(t) in (14) in the BKE discussed in Section 2.7 becomes dramatically aggravated. We consider it in practically important situations, to which Eqns (17) and (19) were addressed. The symbol  $\uparrow$  can now denote either a sharp switching on of the FP (torque)  $x = \text{const or a smooth switching on during the time interval <math>\delta t$ , smaller than the rotor period of revolution for a given x.

Now,  $E(t) \approx x \Delta Q(t)$ , and  $\Delta Q(t) = Q(t) - Q(0)$  increases with time without a bound, approximately linearly on average, if the external force is balanced by viscous resistance of the liquid. In this regard,  $E(t) \approx x \Delta Q(t)$  represents the energy dissipated by the system in a (quasi-)steady nonequilibrium state. Analogous dissipative states arise, for example, when x is an electric potential applied to a conductor, or the force (electric field) acting on a particle (charge carrier) in an unbounded medium (in the thermodynamic limit), while  $\Delta Q(t)$  is the transported charge or particle displacement. In all such situations, BKE (12) or (17) reveals definite rigid connections between generally nonlinear dissipation (rheological properties of a liquid, current-voltage characteristics of a conductor, particle mobility, etc.) and statistical characteristics of fluctuations of dQ(t)/dt (the angular velocity of a rotor, electric current, particle velocity, etc.), while E(t) continuously accumulates new experimental information for these connections.

By contrast, the quantity  $W(t > \delta t) \approx -xQ(0) = \text{const}$ , as in Section 2.7, remains constant in time, giving no information about nonequilibrium processes in the system [moreover, even about Q(0), because in OSs any value Q(0)can be made the reference point for Q(t) by setting Q(0) = 0]. To extract a portion of the information about the dissipated energy E(t) from W(t), at least for a single time instant, as in Section 2.7, we have to retract the force x to zero for a time, i.e., arrange an artificial 'cyclic process' and thus disturb the state under investigation. Moreover, according to Section 2.7, because of the continuous growth of  $\Delta Q(t) \propto t$  with time, the return to zero becomes a less and less correct operation, requiring a more and more precise measurement of x, with an error  $\sim T/\langle \Delta Q(t) \rangle = xT/\langle E(t) \rangle$ . An attempt to continuously extract information about the dissipative state from W(t) and the JE would result merely in the elimination of this state (which is the genuine price of the 'equivalence' of JEs and BKEs in 'cyclic processes'!).

# **2.10** Evolution of nonequilibrium states and thermodynamic inequalities

We consider a CS that at t = 0 is in a nonequilibrium state. We can try to model the corresponding distribution  $D(\Gamma; t = 0)$  by an equivalent 'quasi-equilibrium' one,

$$D_{\rm qe}(\Gamma, X) = \exp\left\{\beta F'(X) - \left[\beta H_0(\Gamma) + XQ(\Gamma)\right]\right\}, \quad (21)$$

where  $\beta = 1/T$ ,  $H_0(\Gamma)$  is an eigen-Hamiltonian of the system (in the absence of external perturbations),  $Q(\Gamma)$  is a suitable set of its individual or collective variables, X is the conjugate set of parameters ('thermodynamic forces') characterizing the system nonequilibrium, and the 'free energy' F'(X) is determined by the normalization condition. The equivalence means that the average values of all the  $Q(\Gamma)$  over the factual and quasi-equilibrium distributions coincide. This requirement determines all X. The variables  $Q(\Gamma)$  can represent spatial inhomogeneities of the densities of particle numbers, mass, charge, momentum, energy, etc. The motivation for such a quasi-equilibrium model is that distribution (21) provides the information entropy maximum in the system with the given mean values of  $Q(\Gamma)$ .

To extend this model to other time instants, that is, to the system evolution, it is natural to rely on formally exact statistical equalities. One of them, similar to BKE (12), follows from identity (7) with  $D_1(\Gamma) = D_2(\Gamma) = D_{qe}(\Gamma, X)$ . Namely, with the possible influence of external forces (fields) conjugate to some of the variables  $Q(\Gamma)$ , we obtain

$$\langle \exp(-\Delta S(t)) \rangle = 1,$$
 (22)

where angular brackets stand for averaging over the quasiequilibrium initial distribution and

$$\Delta S(t) = \beta E(t) + X (Q(t) - Q(0))$$
  
=  $\int_0^t (\beta x(t') + X) \frac{dQ(t')}{dt'} dt'.$  (23)

This quantity can usually be treated as a change, or increment, of the entropy of the system in the course of its evolution.

In [10–13, 32], it was shown that statistical equalities and FDRs associated with quasi-equilibrium ensembles of microstates form a reliable base for nonlinear nonequilibrium thermodynamics. This is evident already from their simple consequences such as 'thermodynamic inequalities'.

It is well known that for any random quantity A, the inequality  $\langle \exp A \rangle \ge \exp \langle A \rangle$  holds. Replacing A by -E here, with E from (13) or (14), and combining this inequality with (12), it is not difficult to conclude that  $\langle E \rangle \ge 0$ . Hence, if a system was initially in equilibrium, it always on average (over a statistical ensemble) takes (from sources of external forces) and absorbs a positive amount of energy.

We now let a system be initially nonequilibrium, as above. Then equality (22) implies the inequality  $\langle \Delta S \rangle \ge 0$ . It allows negative values of the mean  $\langle E \rangle$ , and therefore the system is able to produce (useful) work against its environment, with  $-\langle E \rangle > 0$ . Then the inequality  $\langle \Delta S \rangle \ge 0$  together with (23) establishes a constraint on the value of this work, dependent on the degree of the system initial nonequilibrium.

We next proceed to statistical equalities, including timereversed processes, and demonstrate that they also obey the comparative characterization presented in Section 2.2 of 'old' (our [8, 9, 11]) and 'new' (Crooks [4–6]) results.

# 3. Time reversibility of microscopic dynamics and generalized fluctuation-dissipation relations

# 3.1 Time reversal

In classical mechanics, time reversibility of motion means that any phase trajectory of a system can be traced backward in time, if at some time instant  $\theta$  the signs of all momenta (velocities) are reversed. In a nonautonomous system, time dependences of external forces and conditions must also be reversed and the signs of some of them ('odd' parameters) must be reversed; in particular, the sign of the magnetic field and, under observations in a rotating frame (e.g., on Earth's surface), the sign of the Coriolis force. The parities  $\epsilon = \pm 1$  of the corresponding Hamiltonian parameters with respect to time reversal are determined by the requirement that  $H(\overline{\Gamma}, x) = H(\Gamma, \epsilon x)$ , where  $\overline{\Gamma} \equiv \{q, -p\}$ . If it is satisfied and the 'forward' time dependence of a current microscopic state of the system,  $\Gamma(t)$ , on its initial state  $\Gamma(0)$  and on external conditions is expressed by a functional  $\Gamma(t) = \mathcal{T}_t \{ \Gamma(0); x(\tau) \},\$ then in the time-reversed view,  $\Gamma(t) = \overline{\mathcal{T}}_{\theta-t} \{\overline{\Gamma}(\theta); \epsilon x(\theta-\tau)\}.$ Equivalently,  $\overline{\Gamma}(\theta - t) = \mathcal{T}_t \{\overline{\Gamma}(\theta); \epsilon x(\theta - \tau)\}$ , where t represents the reversed time counted backward from the 'turning point'  $\theta$ .

Accordingly, the observation of any variable  $Q(\Gamma)$  that has a definite parity,  $Q(\overline{\Gamma}) = \varepsilon Q(\Gamma)$  ( $\varepsilon = \pm 1$ ), instead of  $Q(t) = Q(\Gamma(t))$  on a forward trajectory, gives  $Q(\overline{\Gamma}(\theta - t)) = \varepsilon Q(\theta - t)$  on the reversed trajectory.

#### 3.2 Generalized fluctuation-dissipation relations

We let  $\Phi{\Gamma(\tau)}$  be some functional of phase trajectories of a system, and consider its mean value in the ensemble of trajectories, defined by canonical initial distribution (5) with parameters x = a:

$$\langle \Phi \{ \Gamma(\tau) \} \rangle_{a,x(\tau)} = \int \Phi \{ \Gamma(\tau) \} D_{eq}(\Gamma,a) \, \mathrm{d}\Gamma.$$

Here, the subscript at the angular brackets reminds us about the initial distribution and external conditions at which the system evolves. Along with this mean, we consider

$$\int \Phi\{\Gamma(\tau)\} \exp\left(\ln \frac{D_{eq}(\Gamma(\theta), b)}{D_{eq}(\Gamma, a)}\right) D_{eq}(\Gamma, a) d\Gamma$$
$$= \int \Phi\{\Gamma(\tau)\} D_{eq}(\Gamma(\theta), b) d\Gamma.$$
(24)

The integrand here differs from the one in the left-hand side of (8) by the extra factor  $\Phi\{\Gamma(\tau)\}$  only. In the right-hand side of (24), as in Section 2.3, we pass from  $\Gamma$  to new integration variables  $\Gamma(\theta)$ , and then from them to  $\overline{\Gamma}(\theta)$ , and apply the Liouville theorem. After that, we express the phase trajectory via  $\overline{\Gamma}(\theta)$  while going to the reversed time, as was described in

Section 3.1. Moreover, we change the notation for the integration variable  $\overline{\Gamma}(\theta)$  to  $\Gamma$  and take into account that  $D_{eq}(\overline{\Gamma}, b) = D_{eq}(\Gamma, \epsilon b)$ . As a result, we obtain the equality

$$\left\langle \Phi\left\{\Gamma(\tau)\right\} \exp\left(-\frac{H(\Gamma(\theta), b) - H(\Gamma, a)}{T}\right)\right\rangle_{a, x(\tau)} = \exp\left(-\frac{F(b) - F(a)}{T}\right) \left\langle \Phi\left\{\overline{\Gamma}(\theta - \tau)\right\}\right\rangle_{\epsilon b, \epsilon x(\theta - \tau)}.$$
 (25)

At  $\Phi\{\ldots\} = 1$ , it reduces to identity (8).

By choosing the shape of the functional  $\Phi\{\ldots\}$  and parameters *a* and *b* in a proper fashion, it is easy to transform (25) into various FDRs for characteristic and probability functionals or statistical moments of the system variables. In view of the arbitrariness of  $\Phi\{\ldots\}$ , equality (25) by itself is equivalent to a visually similar relation for the density of the probability measure in the space of phase trajectories described with sufficient completeness (specification). This presumes that a set of variables  $V(t) = V(\Gamma(t))$  used in a 'coarse-grained' description allows expressing the difference  $H(\Gamma(\theta), b) - H(\Gamma, a)$  (although it can otherwise be arbitrarily small or rough in comparison with  $\Gamma(t)$ ). In addition, it follows from Section 2.2 that the parameters *a* and *b* must be chosen in accordance with Table 2.

Table 2. Permissible parameter values for open and closed systems.

Open system	Closed system		
	FP	PP	
a = b = 0	Any <i>a</i> , <i>b</i>	$a = x(0), b = x(\theta)$	

In the case of CS–FP, any a and b are allowed, but nevertheless, as in Sections 2.4 and 2.5, for the JE and BKE derivations, we confine our consideration to the two particular variants from neighboring entries of Table 2.

Thus, when considering CSs and taking a and b from the third column of Table 2, instead of (25) we can write

$$\mathcal{P}[V;x]\exp\left(-\frac{W(\theta)}{T}\right) = \exp\left(-\frac{\Delta F(\theta)}{T}\right)\mathcal{P}[\tilde{V};\tilde{x}],\quad(26)$$

where  $\mathcal{P}[V; x]$  is the density of the probability distribution of possible observations (trajectories) of  $V(\tau)$  with given variations of the parameters  $x(\tau)$  ( $0 \le \tau \le \theta$ ),  $\Delta F(\theta) =$  $F(x(\theta)) - F(x(0))$ ,  $\tilde{V}(\tau) = \varepsilon V(\theta - \tau)$ ,  $\tilde{x}(\tau) = \epsilon x(\theta - \tau)$ , and the quantity  $W(\theta)$  [change (11) of the system total energy] is assumed to be expressed in terms of  $V(\tau)$ , that is, the variables Q(t) conjugate to x(t) are contained in the set V(t) or are functions of V(t). This formula is equivalent to the Crooks equality [1, 4–7].

When considering OSs, we have to take a and b from the first column of Table 2, which leads from (25) to

$$P[V;x]\exp\left(-\frac{E(\theta)}{T}\right) = P[\tilde{V};\tilde{x}].$$
(27)

Here, P[V; x] has the same meaning as above, and the quantity  $E(\theta)$  [change, (13) or (14), of the system internal energy] is also assumed to be expressed in terms of  $V(\tau)$ . For this, it is more than sufficient that the Hamiltonian of the system–environment interaction  $-h(\Gamma, x)$  be written in the form  $-h(V(\Gamma), x)$  [for instance, in the bilinear case in (4), Q(t)

are again either some of V(t) or some functions of them]. This formula is equivalent to formula (7) in [8] and some formulas in [9, 11, 12].

The probabilities in (26) and (27) are denoted by different symbols because equalities (26) and (27) pertain to different statistical ensembles and different types of systems in general. Among themselves, they relate nearly like the JE and BKE do (see Section 2.7). Namely, (26) can be applied to OSs, and (27) to CS–PP, under the condition  $x(\theta) = x(0) = 0$  only, and then they formally coincide with one another. In the CS–FP case, the two equalities work simultaneously and supplement one another, although they are mutually connected (as we show in Section 3.3).

It is easy to generalize equality (27) to the quasiequilibrium statistical ensemble described in Section 2.10 by substituting distribution (21) in place of (5) in (24). As a result, in addition to (22), we obtain

$$P[V; x, X] \exp\left(-\Delta S(\theta)\right) = P[\tilde{V}; \tilde{x}, \tilde{X}], \qquad (28)$$

with  $\Delta S(t)$  defined in (23) and with  $\tilde{X} = \varepsilon X$ .

All three relations (26)–(28) can be unified into a single relation of form (1) if in the first of them we introduce  $\Delta S = E/T$ , in the second  $\Delta S = [W - \Delta F]/T$ , in both of them  $\Pi_+ = \{V; x\}, \Pi_- = \{\tilde{V}; \tilde{x}\}$ , and introduce  $\Pi_{\pm}$  similarly for (28). Moreover, for the 'mixed' systems defined in Section 2.2 (or systems having the FP and PP simultaneously) we have to (or can) write a clear mix of equalities (26) and (27).

#### **3.3 From old to new relations and back**

In the CS–FP cases, the variables V(t) in the 'new' and 'old' relations (26) and (27) can always be identified. The difference between (26) and (27) then reduces to the difference in probability distributions of the initial point  $V_0 = V(0)$  of trajectories  $V(\tau)$ . This means that

$$\mathcal{P}[V;x] = \mathcal{P}[V|V_0;x] \mathcal{D}_{eq}(V_0,x(0)),$$

$$P[V;x] = \mathcal{P}[V|V_0;x] \mathcal{D}_{eq}(V_0,0),$$
(29)

where  $\mathcal{P}[V|V_0; x]$  is the conditional probability distribution of trajectories  $V(\tau)$  common to (26) and (27) with a given initial point, and

$$\mathcal{D}_{eq}(V,a) = \int \delta(V - V(\Gamma)) D_{eq}(\Gamma,a) \,\mathrm{d}\Gamma$$
(30)

are possible equilibrium distributions of the variables V. Indeed, in view of the completeness of these variables, it follows from (5) and (30) that

$$\mathcal{D}_{eq}(V,a) = \mathcal{D}_{eq}(V,0) \exp \frac{F(a) - F(0) + h(V,a)}{T},$$
 (31)

where h(V, a) is the interaction energy from (6) expressed in terms of V [see the comment after (27)]. Using this equality together with decomposition (29) in both sides of (26), after elementary manipulations subject to (15), we arrive at (27). Conversely, going from Eqn (27) the same way but in the opposite direction, we obtain equality (26).

Thus, from a purely formal standpoint, in the field of CS-FP, old and new relations are absolutely equivalent at any time variations of parameters. But from the standpoint of practical applications or tests, they differ from each other as strongly as the JE and BKE do (see Sections 2.7–2.9).

A literal practical realization of each of the two variants of time reversal presumed in (26) and (27) requires preliminary preparation of the system, that is, its thermalization with the corresponding Hamiltonian parameters from Table 2. In variant (27), transition from the preparation of the system to the observation of its evolution can involve jumps of Hamiltonian parameters at the beginning of observation [at least, at the beginning of the reverse process, similarly to example (20)]. But we know from Sections 2.2 and 2.6 that this is entirely legitimate for the FPs, which is especially useful in the case of OSs, when the theory and its applications can practically operate with only the 'old' variant of time reversal and old FDRs (27).

# 3.4 Other fluctuation-dissipation relations for probabilities and fluctuation theorems

If the variables V do not form a complete set, it can be formed merely by adding the integral  $W = W(\theta)$  or  $E = E(\theta)$  to them as a whole. Then, instead of (26) and (27), equality (25) implies

$$\mathcal{P}[V, W; x] \exp\left(-\frac{W}{T}\right) = \exp\left(-\frac{\Delta F}{T}\right) \mathcal{P}[\tilde{V}, -W; \tilde{x}], \quad (32)$$

$$P[V, E; x] \exp\left(-\frac{E}{T}\right) = P[\tilde{V}, -E; \tilde{x}], \qquad (33)$$

where joint probability distributions of  $V(\tau)$  and  $W = W(\theta)$ or  $E = E(\theta)$  appear, and we take into account that values of W and E in mutually time-reversed processes differ by signs only (it is easy to verify this with the help of 'time reversal rules' in Section 3.1).

Integration of (32) and (33) over all trajectories of V yields the relation

$$\mathcal{P}(W; x) \exp\left(-\frac{W}{T}\right) = \exp\left(-\frac{\Delta F}{T}\right) \mathcal{P}(-W; \tilde{x})$$
 (34)

and relation (18) for marginal probability distributions of  $W = W(\theta)$  and  $E = E(\theta)$ . Then, dividing (32) by (34) and (33) by (18), we obtain the relations

$$\mathcal{P}[V|W;x] = \mathcal{P}[\tilde{V}|-W;\tilde{x}], \quad P[V|E;x] = P[\tilde{V}|-E;\tilde{x}] \quad (35)$$

for conditional distributions of  $V(\tau)$  at fixed values  $W = W(\theta)$  or  $E = E(\theta)$ , which here play the role of additional external conditions for observing  $V(\tau)$ .

Relations of form (18) and (34) are currently very popular and are usually termed 'fluctuation theorems' (FTs) [16, 18, 43]. Sometimes they are presented as a big step forward from 'old' results, although it is quite evident that equality (18) is the simplest consequence of (27) produced by (mental) integration of (27) over all  $V(\tau)$ trajectories ( $Q(\tau)$  trajectories in [8]) with a fixed value  $E = E(\theta)$ . Similarly, equality (28), or (1), implies the FT for entropy increments:  $P(\Delta S; x, X) \exp(-\Delta S) = P(-\Delta S; \tilde{x}, \tilde{X})$ .

We in our time wrote and used such relations in slightly different forms more convenient in applications of interest to us, taking into account that the actually measured quantities are usually not E(t) but dQ(t)/dt,  $\Delta Q(t)$ , or others conjugate to external forces. Below in Sections 3.6 and 3.8, it is demonstrated how FT (18) was applied by us to open systems in 1979 in [9] and later.

We note in addition that in application to OSs in (quasi-) steady nonequilibrium states, variant (19) of FT (18) can be

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rewritten as a symmetry relation  $P(\sigma) \exp(-\sigma\theta) = P(-\sigma)$  for time-averaged entropy production  $\sigma = E(\theta)/T\theta$ , and that this kind of relations can appear in non-Hamiltonian dynamic models of dissipative processes [43, 46]. From the standpoint of Hamiltonian statistical mechanics, this is an advantage of such a model, although not a proof of its legitimacy.

## 3.5 Markovian fluctuation-dissipation relations

A set of variables  $V(t) = V(\Gamma(t))$  represents a Markovian random process if their current values determine the probabilities of their future values uniquely and independently of their past. The generalized FDRs are formally compatible with assumptions about Markovian behavior of one set of variables or another, although in a rigorous sense it never occurs (unless  $V(\Gamma)$  coincides with  $\Gamma$ ). This allows formulating general recipes for constructing Markovian 'stochastic models' that fully take all FDRs into account and thus automatically agree with both the time reversibility of microdynamics and the principles of (statistical) thermodynamics of irreversible processes [8, 9-15, 33]. For closed systems with constant parameters, this was already done by Stratonovich [30] (see also [29] and the references therein and in [8, 9, 15]) based on the principle of detailed balance. In [8], we showed that his results can be extended to nonconstant (time-dependent) parameters.

The corresponding 'old' results wholly contain the Crooks theory presented initially as a Markovian one [4, 5].

To verify this, we recall that a Markov process is completely determined by its probabilities of transition from  $V_0 = V(0)$  to  $V_{\theta} = V(\theta)$  in an infinitesimally small time  $\theta \to 0$ . We consider them using the notation  $\mathcal{P}(V_{\theta}|V_0; x)$ . We note that, first, due to the completeness of V(t) (see Section 3.2), at small  $\theta$  in (26),  $W(\theta) \to -dx(\theta) Q_0$ , where  $dx(\theta) = x(\theta) - x(0) \propto \theta$  and  $Q_0 = Q(0)$  [with Q(t) from (11)] are functions of V(0) or components of V(0). Second, it follows from (5) and (31) that

$$\mathcal{D}_{eq}(V_{\theta}, x(\theta)) \to \mathcal{D}_{eq}(V_{\theta}, x(0)) \exp \frac{\Delta F(\theta) + dx(\theta) Q_0}{T}.$$

Inserting these expressions, together with (30), into (26), we see that the exponentials in (26) cancel up to the second order of  $\theta$ , and hence the equality

$$\mathcal{P}(V_{\theta}|V_0; x) \mathcal{D}_{eq}(V_0, x) = \mathcal{P}(\varepsilon V_0|\varepsilon V_{\theta}; \epsilon x) \mathcal{D}_{eq}(\varepsilon V_{\theta}, \epsilon x) \quad (36)$$

holds, with  $x = x(0) \approx x(\theta)$ . It coincides with the principle of detailed balance (PDB) for systems with constant parameters. This just means that the 'Crooks equality' is in essence a time-nonlocal formulation of the 'old' Markovian theory.

In its time-local formulation,

$$\mathcal{P}(V|V_0; x) \to |1 + \theta K(V, \nabla, x)| \,\delta(V - V_0) \,,$$

where  $\nabla = \partial/\partial V$  and transition probabilities in (36) are replaced by the 'kinetic operator'  $K(V, \nabla, x)$  and the kinetic equation

$$\dot{D}(V;t) = K(V,\nabla, x(t)) D(V;t), \qquad (37)$$

in which D(V; t) is the current probability density distribution of the Markovian variables. Here, the role of equality (26) for CSs, that is, the role of PDB (36) is played by the operatorvalued symmetry relation

$$K(V, \nabla, x) \mathcal{D}_{eq}(V, x) = \mathcal{D}_{eq}(V, x) K^{\dagger}(\varepsilon V, \varepsilon \nabla, \epsilon x), \qquad (38)$$

which accumulates all the consequences of microscopic reversibility and FDRs. Here,  $\dagger$  is the symbol of conjugation, or transposition, in the Sturm–Liouville sense. The operator *K* can be a differential operator (for example, in Fokker–Planck equations) or an integral operator (for example, in Kolmogorov equations). We note that FDRs, in combination with the causality principle, forbid any *K* dependence on time variations of parameters except an instant one, i.e., the dependence on their current values only (but in no way on past values) [8].<sup>6</sup> Stationary solutions of kinetic equation (37) (at constant parameters) are equilibrium distributions  $\mathcal{D}_{eq}(V, x)$  in (30).

In 1978–1981, we suggested generalizing this Markovian theory to open systems [9, 11–15, 33]. Of course, the generalization must be guided by relation (27) [or (28)]. In the simplest Markovian models of OSs, the set of variables  $V(t) = V(\Gamma(t))$  is complete, and they therefore allow expressing the dissipated power (energy dissipated by the system per unit time), i.e., the integrand in (13) or (14) [for which even a single variable, e.g., I(t) = dQ(t)/dt, may be sufficient]. Then, instead of (38), we obtain an essentially different operator-valued relation,

$$K(V, \nabla, x) \mathcal{D}_{eq}(V, 0) = \mathcal{D}_{eq}(V, 0) \left[ K^{\dagger}(\varepsilon V, \varepsilon \nabla, \epsilon x) + \frac{N(V, x)}{T} \right],$$
(39)

where N(V, x) represents the dissipated power [possibly in the form N(V, x) = xI(V)].

Now, the stationary solution (with x = const) of kinetic equation (37) is in equilibrium [equals  $\mathcal{D}_{eq}(V, 0)$ ] at x = 0 only. If  $x \neq 0$ , the stationary solution of (37) describes the above steady nonequilibrium state (see Sections 2.9 and 3.4) with the permanent entropy production  $\langle \sigma \rangle = \langle N(V, x)/T \rangle \neq 0$  as  $E(t)/t \rightarrow T \langle \sigma \rangle$ , and fluctuations of E(t) and other quantities are characterized by a violation of the balance of mutually time-reversed processes.

Of course, from (38) and (39), we can respectively return to (26) and (27). We note once again that for 'mixed' systems, i.e., those having parameters of both closed and open types, instead of equalities (38) or (39), it is necessary to write their obvious hybrid.

# 3.6 Fluctuation-dissipation relations for transport processes

To demonstrate one possible application of the FDRs [particularly, (19) and (27)], we consider charge transport through a conductor under a constant voltage drop x (after switching on at t = 0). Here, the dissipated energy is  $E(\theta) = x\Delta Q(\theta)$ , with  $\Delta Q(\theta) = Q(\Gamma(\theta)) - Q(\Gamma)$  representing the charge transported through the conductor during the observation time.

We combine the exact FDRs and a simple stochastic model of the system. The FDRs are now represented by relation (FT) (18) written in the form

$$P(\Delta Q; x) \exp\left(-\frac{x\Delta Q}{T}\right) = P(-\Delta Q; x), \qquad (40)$$

<sup>6</sup> In general, the causality principle is also a very useful tool for the analysis of consequences of generalized FDRs [8, 9, 11].

factually used in [9], where the probability distribution P is now related to the charge. As regards the model, we assume that our conductor is a contact (like a p-n-junction), and charge is therefore transported through it by discrete portions  $\pm e$  forming two opposite Poissonian random flows. This means that the mean value of the electric current  $\bar{I}(x) = \langle \Delta Q \rangle / \theta$  and the spectral power density of the current noise  $S(x) = [\langle \Delta Q^2 \rangle - \langle \Delta Q \rangle^2] / \theta$  are expressed by the formulas

$$\bar{I} = e[n_+ - n_-], \qquad S = e^2[n_+ + n_-],$$
(41)

in which  $n_{\pm} = n_{\pm}(x)$  are mean numbers of the elementary charge portions transferred per unit time in the forward and backward directions.

Clearly, FDRs establish a connection between  $n_+(x)$  and  $n_-(x)$ . In [9], it was extracted from relations for the characteristic function of  $\Delta Q$  equivalent to (40). Here, we can merely surmise that relation (40) is valid not only for  $\Delta Q$  as a whole but also for elementary transfer events:

$$n_{+}(x)\exp\left(-\frac{ex}{T}\right) = n_{-}(x).$$
(42)

From here and from (41), we obtain the following relation between the power of nonequilibrium noise and the mean current (current–voltage characteristic):

$$S(x) = e\bar{I}(x) \coth \frac{ex}{2T}.$$
(43)

At  $e|x| \ll 2T$ , it reduces to the Nyquist formula for 'thermal noise', while in the opposite case it reduces to the formula for 'shot noise'.

In this way, FDRs help reveal universal connections between the dissipative nonlinearity of a transport process (I(x)), its noise characteristics (S(x)), and the type of its statistics. For the Gaussian statistics, instead of (43), we would obtain  $S(x) = 2T\bar{I}(x)/x$ . More complicated examples of this kind can be found in [9–13, 31, 37–39]. We note that measurements of  $\bar{I}(x)$ , S(x), and higher-order cumulants of  $\Delta Q$  are, in principle, no worse a way of experimental testing of the exact theoretical results in (12), (18), and (40) than the one discussed in [1] and in Section 2.8.

#### 3.7 Fluctuation-dissipation relations for 1/f-noise

The stochastic model just considered has a fundamental defect: in it, elementary random events have the *a priori* prescribed relative frequency (time-averaged number of events per unit time, or their 'probability per unit time')  $n_{\pm}(x)$ , independent of the concrete realization of the experiment, i.e., independent of the phase trajectory of the system, although, as was shown by Krylov many years ago [47], statistical mechanics gives no grounds for such assumptions.

This statement can already be understood on the intuitive level. Indeed, the mentioned assumption would be likely if the system remembered a number of past events and compensated its deviations from the 'norm' by means of an opposite deviation of a number of later events. But this is impossible if the system forgets about events soon after they occur. Then it does not distinguish between 'norm' and 'deviation' and therefore produces fluctuations in the number of events proportionally to its 'normal' (mean) value. This means that the relative frequency of events ('probability per unit time') undergoes low-frequency fluctuations with a 1/f-type spectrum.

A similar reasoning was first suggested and mathematically formulated in [35, 36, 48] and later confirmed on the basis of statistical mechanics in [37–39, 42, 49–55] and other work, first of all in application to random walks ('Brownian motion') of atomic-size particles.

We emphasize that fluctuations ('1/f-noise') of relative frequencies by their very nature do not violate the existing balance (which would set in anyway) or definite disbalance of mutually time-reversed events (processes). Therefore, as follows from the generalized FDR [35–37, 39], various particular FDRs like (42) also hold for fluctuating relative frequencies and all derived 'kinetic' quantities. For example, the Einstein relation  $D = T\mu$  between the diffusivity D and mobility  $\mu$  of a walking particle can be extended to their fluctuations [37] (as well as the Nyquist formula can be extended to fluctuations of conductance and fluctuations of 'instant' spectral power density of 'white' electric noise [35, 39]). To substantiate such statements, relation (40) (formula (A4) from [37]) is quite sufficient.

Therefore, it is possible, as was already suggested in [48], to separate fast fluctuations (white noise) and low-frequency fluctuations (1/f-noise) using primitive phenomenological language but keeping in mind its rigorous statistical-mechanical equivalent. We next consider the statistics of random walk of a probe ('marked') gas particle in this way, based on the results in [37, 41, 51–53].

### **3.8 Fluctuation-dissipation relations** and molecular Brownian motion

In relation (40) ((A4) in [37]), we now let  $\Delta Q$  denote the displacement, or the path, of a 'Brownian particle' (BP). Let *R* be the projection of  $\Delta Q$  on the direction of the external force *x* applied to the BP (a probe gas atom). In the widely known simplest stochastic model of Brownian motion, FDR (FT) (40) is satisfied by the Gaussian distribution

$$P(R;x) = P_{\mu}(R;x) \equiv \frac{\exp\left[-(R - \mu xt)^2 / 4T\mu t\right]}{\sqrt{4\pi T\mu t}}.$$
 (44)

Here, it is assumed, of course, that the observation time *t* is much longer than the BP velocity relaxation time or the mean free path time  $\tau$ .

However, honest consideration of the exact Bogoliubov– Born–Green–Kirkwood–Yvon (BBGKY) equations for an infinite chain of many-particle distribution functions of a fluid shows that expression (44) is incompatible with the absence of (single-time) statistical correlations between the BP and gas atoms at a long distance from it. The true expression (first obtained in [51] and then by a different method in [42, 52]) can be represented by a superposition of Gaussian distributions with various values of the BP mobility:

$$P(R;x) = \int_0^\infty P_\mu(R;x) \, U_t(\mu) \, \mathrm{d}\mu \,, \tag{45}$$

$$U_t(\mu) = \frac{\bar{\mu}^2}{\mu^3} \exp\left(-\frac{\bar{\mu}}{\mu}\right) \Xi\left(\frac{T\mu}{v_0^2 t}\right),\tag{46}$$

where  $\Xi(\cdot)$  is a 'cut-off' function that rapidly vanishes at infinity and is equal to unity at zero,  $\Xi(0) = 1$ , and  $v_0$  is the characteristic thermal velocity of gas atoms (speed of sound). Hence, for variances of the BP path and the dissipated energy E = xR, we have

$$\langle R, R \rangle = 2T\bar{\mu}t + (\bar{\mu}xt)^2 F\left(\ln\frac{t}{\tau}\right),$$
 (47)

$$\langle E, E \rangle = 2T \langle E \rangle + \langle E \rangle^2 F \left( \ln \frac{t}{\tau} \right),$$
 (48)

with  $F(z) \approx z$ . Here and below, the angular brackets with *n* commas inside denote the joint (n + 1)th-order cumulant of n + 1 random quantities separated by the commas ('Mala-khov's cumulant brackets' [54]). The second terms in (47) and (48) respectively describe 1/f-fluctuations of mobility and dissipated power. At x = 0, a similar asymptotic expression characterizes the fourth-order cumulant of *R*, thus reflecting identical fluctuations of the BP diffusivity  $D = T\mu$  [35, 39, 48–50].

The function  $U_t(\mu)$  in (46) is the effective BP mobility probability distribution. Its long power-law tail is typical for distributions accompanying 1/f-noise [36, 48–50]. At  $\langle E \rangle = \bar{\mu}x^2t \gtrsim T$ , this cubic tail manifests itself in path distribution (45) on the right (if x > 0):  $P(R; x) \approx \langle R \rangle^2 / R^3$ for  $R > \langle R \rangle$ . Accordingly, a similar tail appears in the distribution of dissipated energy in (18):  $P(E; x) \approx \langle E \rangle^2 / E^3$ for  $E > \langle E \rangle$ . Hence, the probabilities of 'large deviations' of the path and dissipated energy are highly maintained in comparison with those predicted by Gaussian model (44). Such distributions have been observed many times in experiments with nonstationary photocurrents (charge injection currents) [55].

It is interesting that the shortest way to these results is to use the FDR [42] (although they can also be easily derived from explicit virial expansions of nonequilibrium partition functions [53]). In (25) with a = b = 0, we set

$$\Phi\big\{\Gamma(\tau)\big\} = \delta\big(Q(t) - R\big)\,\delta(Q)\prod_k (1 + \phi(q_k))\,,$$

where  $\phi(q)$  is some function of atom coordinates and the product is taken over all gas atoms (except the BP itself). Then the left-hand side of (25) characterizes the influence of the initial spatial nonuniformity of the gas on the BP walk, while the right-hand side describes statistical correlations between the BP path (during the entire observation time) and the current microstate of the gas (in configuration space). Further, choosing the function  $\phi(q)$  properly, we can extract the relation

$$v \frac{\partial P(R;x)}{\partial v} = P(R;x) \int \left[ v(\rho|R;x) - v \right] d^3\rho$$
(49)

from (25), where v is the mean particle number density in the gas and  $v(\rho|R; x)$  is the conditional mean value of gas density at the distance  $\rho$  from the BP at a given path.

It follows from (49) that

$$\frac{\partial \ln P(R;x)}{\partial \ln v} > -v\Omega, \qquad (50)$$

where  $\Omega$  is the characteristic spatial volume to which correlations of the gas with the BP extend. On the other hand, in Gaussian model (44) with the known dependence  $\mu \propto D \propto 1/\nu$ , we have

$$\frac{\partial \ln P_{\mu}(R;x)}{\partial \ln v} = \frac{1}{2} - \frac{\langle E \rangle}{4T} \left[ \left( \frac{R}{\langle R \rangle} \right)^2 - 1 \right]$$

Comparing this expression with inequality (50), we see that they are incompatible if the 'correlation volume'  $\Omega$  is bounded above by a finite number. Hence, if the gas stays indifferent to (forgets about) the outcome *R* of the BP walk, it is unable to suppress large values of *R* as categorically as law (44) requires.

At the same time, laws (45) and (46) are compatible with (50) at  $\Omega = 2/v$ . Of course, this (or another) value of  $\Omega$  cannot be obtained from FDRs themselves only: its calculation requires the whole BBGKY hierarchy [37, 51] or equivalent means (see [52, 53] and the references in [53]).

### 3.9 Variance of dissipation fluctuations

The preceding paragraph gave an example of large fluctuations of dissipation whose magnitude, according to (48), is of the order of the mean dissipation value. Another such example was considered in [38]. If energy is dissipated through not one but many ( $N \ge 1$ ) degrees of freedom, then the variance of dissipation fluctuations, along with the magnitude of the power-law tail of their distribution, is approximately N times smaller. For systems with Hamiltonians of type (4), we can obtain [38] the exact FDR

$$\langle E \rangle = \frac{1}{T} \int_{1>2} x(1) \langle I(1), I(2) \rangle_{x(\tau) \eta(\tau-2)} x(2) \, \mathrm{d}1 \, \mathrm{d}2 \,, \qquad (51)$$
  
 
$$\langle E, E \rangle = 2T \langle E \rangle + \frac{2}{T} \int_{1>2>3} x(1) \, x(2)$$
  
 
$$\times \left\langle I(1), I(2), I(3) \right\rangle_{x(\tau) \eta(\tau-3)} x(3) \, \mathrm{d}1 \, \mathrm{d}2 \, \mathrm{d}3 \,, \qquad (52)$$

where the numbers replace literal time arguments (and their indices), I(t) = dQ(t)/dt are 'currents' conjugate to the external forces x(t), and  $\eta(t)$  is the Heaviside step function. Its presence means that in second- and third-order cumulants in the integrands, the earliest (right-hand) values of the 'currents' I(t) [i.e., I(2) and I(3), respectively] belong to a still undisturbed (equilibrium) system. These equalities follow from the general FDR for cumulants [9, 11] (importantly, as we already mentioned in Section 2.2, paper [11] contains two variants of such FDRs, which together cover both types of systems and both types of parameters).

In many applications, the third-order cumulant in (52) (or the result of its integration) can be assumed to vanish at x = 0. Then, under a weak perturbation,

$$\langle E, E \rangle = 2T \langle E \rangle + \frac{2}{T} \int_{2>3,4}^{1>4} x(1) x(2) \times \langle I(1), G(2,3), I(4) \rangle_0 x(3) x(4) \, d1 \, d2 \, d3 \, d4 \,,$$
 (53)

where  $G(2,3) = [\delta I(2)/\delta x(3)]_{x=0}$  is the dynamical differential linear response (introduced at the level of microscopic dynamics) of the currents to the forces [38], the first term is proportional to  $x^2$ , and the second to  $x^4$ . But the second term does not reduce to a mere small correction if it grows with the observation time faster than linearly. For instance, in (48), it increases roughly proportionally to  $t^2$ . Then the integral in (53) describes the contribution from equilibrium 1/f-fluctuations of kinetic coefficients of the system. As can be seen from (53) (and was demonstrated in [38, 56]), they are naturally related to fluctuations of the differential response  $\delta I(2)/\delta x(3)$ , characterizing the exponential instability of system phase trajectories with respect to their small perturbations [45, 47, 57].

# 4. Conclusion

We have presented our view of the generalized fluctuation– dissipation relations (FDRs), or theorems, first introduced by us in 1977, in comparison with analogous results that appeared in 1997 and later. They all manifest the conservation of phase space volume under microscopic dynamic motion and its time symmetry (reversibility), both essentially determining statistical and dissipative properties of thermodynamically nonequilibrium physical systems.<sup>7</sup>

The comparison gave us sufficient reasons to say, in contrast to the misunderstandings observed in related literature (see the Introduction), that 'new' results have not introduced a principal novelty or greater generality, in essence appearing as alternative formulations of the 'old' results. Our approach suggested in our time (and reflected in this paper) has a more general character, allowing us to note and use qualitative peculiarities of different types of systems, first of all on the level of their Hamiltonians and statistical ensembles, and then their stochastic models. In the framework of our approach, it is easy to see inter-connections of the new and old results, possibilities of choosing the most appropriate form of FDRs for concrete application, and the derivation of new variants of FDRs not considered previously.

On the whole, generalized FDRs deliver all the necessary tools for the construction of thermodynamically correct models of real nonequilibrium processes and systems. Regardless of the degree of complexity or roughness of a model, observance of FDRs at its level ensures its qualitative agreement with rigorous statements of statistical mechanics (and sometimes even closely leads to quantitative agreement, as was demonstrated, in particular, by the examples in Section 3). This useful potential of FDRs will not likely become exhausted some day.

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<sup>7</sup> In the context of FDRs, the word 'thermodynamic' and its derivatives refer mainly to statistical ensembles but not sizes of systems of interest, and hence the generalized FDRs are equally valid for both large systems (even with infinitely many degrees of freedom) and small ones (even with a single degree of freedom).

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