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RECIPROCAL RELATIONS FOR CHEMICAL OSCILLATORS

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Earlier [V. P. Lesnikov, Ukr. J. Phys. **64**, 126 (2019)] it was pointed out that for thermal hydrodynamic fluctuations in open hydrodynamic steady states (OHSS) the determining factor for derivation of reciprocal relations is not the principle of microscopic reversibility, but the presence or absence of a flux. In the present work this idea is applied to open chemical steady states (OCSS), where chemical oscillations are possible. The behavior of concentration fluctuations when there are no macroscopic oscillations yet is considered. The reciprocal relations for such OCSS are found.

Key words: open chemical steady state (OCSS), chemical oscillators, concentration fluctuations, reciprocal relations.

I. INTRODUCTION

Reciprocal relations established by Onsager follow from even parity of two-time correlation functions of macroscopic fluctuations [2, 3]. Later Casimir showed that the corresponding correlation functions can be not only even, but also odd [4]. As a result, the Onsager–Casimir reciprocal relations arose. The equality expressing a definite parity of two-time correlation functions is called the detailed balance.

To explain the detailed balance, Onsager put forward the principle of microscopic reversibility, according to which macroscopic quantities are functions of the canonical coordinates of the microparticles of matter. The parity with respect to time reversal of the macroscopic quantity depends on the parity of these functions. If both macroscopic quantities included in the correlation function have the same parity, then the correlation function is even. If the parity of the corresponding quantities is different, then the correlation function is odd. The kinetic coefficients will also have the same symmetry.

This explanation led to the belief that the Onsager–Casimir reciprocal relations cannot be derived within the phenomenological thermodynamics and can be deduced only using statistical physics because they are a consequence of the reversibility of microscopic dynamics [5, 6]. In this regard, it was assumed that the Onsager–Casimir reciprocal relations should always hold. In particular, this was a mandatory requirement for the study of thermodynamic (hydrodynamic) fluctuations in open hydrodynamic steady states (OHSS) that began in the last century.

It is clear that open systems with stationary fluxes are non-equilibrium. For these systems, the requirement to fulfill the Onsager–Casimir reciprocal relations led to contradictory results in the calculation of two-time correlation functions of fluctuations performed using different and seemingly mathematically equivalent methods [7–9]. All contradictions are eliminated if, in order to explain the Onsager–Casimir reciprocal relations, we replace the principle of microscopic reversibility with a completely thermodynamic condition, i. e. that is absence of fluxes. This statement means that the Onsager–Casimir reciprocal relations are satisfied only in equilibrium systems, and are not related to non-equilibrium ones. The flux breaks the detailed balance and temporal symmetry and we will have completely different reciprocal relations. To do this, remaining within the framework of thermodynamics, it is sufficient to know only the dynamics of fluctuations and their locally equilibrium distribution function of the initial values.

In this paper, we apply the above idea to chemical oscillators. Chemical reactions represent an important branch of non-equilibrium thermodynamics [10]. The OCSS have such interesting phenomena as oscillations, spatial structures, waves, chaos. All of them must be described on the basis of thermodynamics, since the main characteristic of any reaction is the concentration of chemical species, which is a macroscopic variable same as temperature, pressure, etc.

II. THEORY OF THERMODYNAMIC FLUCTUATIONS IN NON-EQUILIBRIUM STEADY STATES

The theory of fluctuations in non-equilibrium systems with fluxes differs from the theory of equilibrium fluctuations precisely by the violation of the Casimir–Onsager reciprocal relations [1, 11]. It is based on only two hypotheses. That is Onsager's regressive hypothesis that dynamics of fluctuations occurs on macroscopic laws and that is the hypothesis of local equilibrium, which is general for a continuous medium in thermodynamics.

Linear stability theory gives the dynamics of small fluctuations

$$\dot{x_i} = -\lambda_{ij} x_j, \tag{1}$$

where here and below we use the notation and definitions adopted in [12].

The probability density of initial fluctuations in the steady state will be

$$w(\mathbf{x}) \propto e^{\Delta S} = \exp\left(-\frac{1}{2}\beta_{ij} x_i x_j\right), \tag{2}$$

where ΔS determines fluctuation deviation from the maximum value S_0 of entropy corresponding to the steady state. Here entropy is a dimensionless quantity, and temperature is measured in energy units.

For the derivatives $X_i = -\partial S/\partial x_i$ we have

$$X_i = \beta_{ij} x_j. \tag{3}$$

The averaging with (2) gives

$$\langle x_i x_k \rangle = \beta_{ik}^{-1}, \quad \langle x_i X_k \rangle = \delta_{ik}, \quad \langle X_i X_k \rangle = \beta_{ik}. \tag{4}$$

Equation (1) can be represented now in the form

$$\dot{x}_i = -\gamma_{ij} X_j. \tag{5}$$

The quantities γ are called kinetic coefficients. Also the notation L is often used for them. From (1), (3), and (5) it follows

$$\gamma_{ij} = \lambda_{ik} \beta_{kj}^{-1}. \tag{6}$$

As explained above, the Casimir–Onsager reciprocal relations

$$\gamma_{ij} = \pm \gamma_{ji} \tag{7}$$

are a consequence of the temporal symmetry condition substantiated by the principle of microscopic reversibility:

$$\langle x_i(t) x_j \rangle = \pm \langle x_j(t) x_i \rangle. \tag{8}$$

Indeed, if we differentiate (8) and set $t = 0$, then we obtain (7). In fact, the opposite is true. Equation (8) does not determine (7), but the kinetic coefficients found from (6) determine the parity of the two-time correlation functions or its absence.

It is easy to find reciprocal relations in the case of two variables in (1) and (2) that will be needed later. It was done in work [1]. It is necessary to solve the Cauchy problem for equations (1) and use the second formula in (4). We have the following result for $i \neq j$ and $\lambda_{ij} \neq 0$:

$$\frac{\langle x_i(t) X_j \rangle}{\langle x_j(t) X_i \rangle} = \frac{\lambda_{ij}}{\lambda_{ji}}. \tag{9}$$

If the initial values are not correlated, i. e. matrix β is diagonal, then we get

$$\frac{\langle x_i(t) x_j \rangle}{\langle x_j(t) x_i \rangle} = \frac{\gamma_{ij}}{\gamma_{ji}} \tag{10}$$

here $\gamma_{ij} = \lambda_{ij} \beta_{jj}^{-1}$.

Formula (10), despite being just a special case of common reciprocal relations (9), turns out to be important for chemical reactions, since, as will be shown below, the initial values of chemical reagents do not correlate with each other.

Equations (1), (2) determine the random Ornstein–Uhlenbeck process. We can calculate correlation functions of fluctuations directly solving the Cauchy problem and then using averaging (2). The equivalent calculation methods are fluctuation-dissipation theorems (FDT) — the first (Callen–Welton) and the second (Langevin). The first FDT follows from the definition of susceptibility. Most used in the study of non-equilibrium fluctuations is the second FDT. In that case, the solution of a homogeneous system of equations (1) is replaced by with the solution of inhomogeneous equations by adding to the right side fluctuating forces y_i with correlation functions

$$\langle y_i(t) y_j(0) \rangle = Q_{ij} \delta(t). \tag{11}$$

The intensity Q is determined by the formula named Langevin FDT

$$Q_{ij} = \gamma_{ij} + \gamma_{ji}. \tag{12}$$

In work [11], it was shown that the FDT are mathematical theorems, the use of which leads to the same results as the solution of the Cauchy problem for (1) upon averaging (2) without any statistical justification for the kinetic coefficients. They are defined in thermodynamics only by formula (6) without imposing any restrictions on them. It should be emphasized that it fully concerns chemical reactions.

Note that for chemical reactions, the method of obtaining intensities by using the shot noise theory [13, 14] is still thriving. The output in [15–17] is the master equation for the distribution function of the number of particles. The number of particles is supposed to increase or decrease by one in the course of the reaction. The distribution function in the master equation is expanding into a power series with respect to "1". This gives the Fokker–Planck equation from which follow the expressions for the intensities.

This approach is not thermodynamic, since, the used macroscopic rate equations describe on the one hand the dynamics of changing a large number of particles, and, on the other hand, the birth-death processes for changing on one particle. Within the framework of thermodynamics, the Fokker–Planck equation for the process (1), (2), as it is easy to show, cannot give anything except (12).

III. RECIPROCAL RELATIONS FOR THE LOTKA OSCILLATOR

For any chemical reactions, we can write the rate equations. In a well stirred system, the solution of these equations is sought in the form of the sum of steady-state concentrations $[X_i]_S$ and concentration fluctuations x_i. In this way, the rate equations give us a matrix λ in (1).

At a steady state, concentrations of the order 1M are typical for chemical reactions. Therefore, reagent particles behave like a rarefied gas. In this case, statistical properties of each variable are obviously specified by $[X_i]_S$. So the matrix β is diagonal with entries $N_A V [X_i]_S^{-1}$ and the inverse matrix β^{-1} that gives one-time correlation functions of fluctuations is also diagonal with entries $\frac{[X_i]_S}{N_A V}$. Here N_A is the Avogadro number, and V is the volume in liters.

In 1910, Lotka predicted the possibility of damped chemical oscillations [18]. His chemical oscillator is described by the reaction scheme

$$\xrightarrow{k_0} X,$$
$$X + Y \xrightarrow{k_1} 2Y, , \qquad (13)$$
$$Y \xrightarrow{k_2},$$
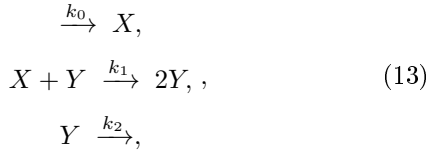
where substance X is formed, say, from substance A, which is an excess, and substance Y is removed from the reaction reservoir turning into B. In (13) k_0, k_1, k_2 are rate constants. The result of the reaction is the formation of a substance B and the consumption of a substance A. So the net reaction is $A \to B$. The flow of matter makes the system non-equilibrium.

The kinetics of the Lotka model is described by the rate equations:

$$\frac{d[X]}{dt} = k_0 - k_1[X][Y],$$
$$\frac{d[Y]}{dt} = k_1[X][Y] - k_2[Y]. \qquad (14)$$

The steady state concentrations will be equal

$$[X]_S = k_2/k_1, \quad [Y]_S = k_0/k_2. \qquad (15)$$

For concentration fluctuations, we obtain the equations

$$\dot{x} = -\frac{k_1 k_0}{k_2} x - k_2 y,$$
$$\dot{y} = \frac{k_1 k_0}{k_2} x. \qquad (16)$$

Equations (16) describe damped fluctuation oscillations with damping coefficient $\delta = k_1 k_0/(2k_2)$ and frequency $\sqrt{k_1 k_0 - \delta^2}$. The expressions for one-time correlation functions of fluctuations are

$$\langle x^2 \rangle = \frac{[X]_S}{N_A V}, \quad \langle xy \rangle = 0, \quad \langle y^2 \rangle = \frac{[Y]_S}{N_A V}. \qquad (17)$$

So

$$\lambda = \begin{pmatrix} \frac{k_1 k_0}{k_2} & k_2 \\ -\frac{k_1 k_0}{k_2} & 0 \end{pmatrix}, \quad \beta^{-1} = \frac{1}{N_A V} \begin{pmatrix} [X]_S & 0 \\ 0 & [Y]_S \end{pmatrix} . \qquad (18)$$

For the kinetic coefficients we get

$$\gamma = \frac{k_0}{N_A V} \begin{pmatrix} 1 & 1 \\ -1 & 0 \end{pmatrix}. \qquad (19)$$
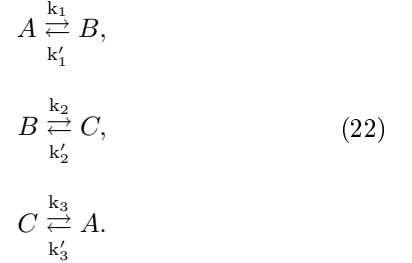
The variables x and y have the same parity. According to the Casimir–Onsager reciprocal relations, there should be $\langle x(t)y \rangle = \langle y(t)x \rangle$ and $\gamma_{12} = \gamma_{21}$. Instead, however, according to (10) we get

$$\langle x(t)y \rangle = - \langle y(t)x \rangle \qquad (20)$$

and

$$\gamma_{12} = -\gamma_{21}. \qquad (21)$$

To demonstrate the principle of microscopic reversibility in chemical reactions, Onsager, in his work [2] used as an example a monomolecular triangle reaction

$$A \underset{k_1'}{\overset{k_1}{\rightleftarrows}} B,$$
$$B \underset{k_2'}{\overset{k_2}{\rightleftarrows}} C, \qquad (22)$$
$$C \underset{k_3'}{\overset{k_3}{\rightleftarrows}} A.$$

The rates of change of amounts n_A, n_B, n_C are given by the equations

$$\dot{n_A} = -(k_1 + k_3')n_A + k_1' n_B + k_3 n_C,$$
$$\dot{n_B} = k_1 n_A - (k_2 + k_1')n_B + k_2' n_C, \qquad (23)$$
$$\dot{n_C} = k_3' n_A + k_2 n_B - (k_3 + k_2')n_C.$$

From (23) it follows that the total amount $n_A + n_B + n_C$ is conserved. This means that the system is closed. The net reaction is zero. So, the system is equilibrium and that is because the Casimir–Onsager reciprocal relations hold here.

IV. THE BRUSSELATOR AND OTHER CHEMICAL OSCILLATORS

The most famous model of a chemical oscillator is the Brusselator, representing a trimolecular collision and an autocatalytic step, given by

$$A \xrightarrow{k_1} X,$$
$$B + X \xrightarrow{k_2} Y + D,$$
$$2X + Y \xrightarrow{k_3} 3X, \qquad (24)$$
$$X \xrightarrow{k_4} E.$$
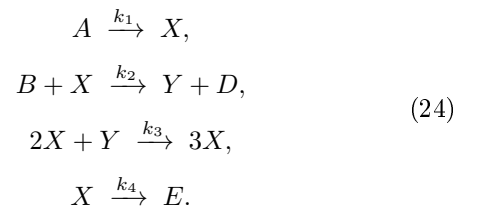
The concentrations $[A]$ and $[B]$ are maintained and the system is assumed to be well stirred. The concentration products $[D]$ and $[E]$ are removed as they are formed. The net reaction is $A + B \to D + E$. So, there is a flow of matter and the system is non-equilibrium.

From rate equations for species X and Y, it is easy to find stationary solutions and matrix λ of linear equations for concentration fluctuations [10]. They look like

$$[X]_S = \frac{k_1}{k_4}[A], \quad [Y]_S = \frac{k_4 k_2}{k_3 k_1} \frac{[B]}{[A]}, \qquad (25)$$

$$\lambda = \begin{pmatrix} k_4 - k_2[B] & -k_3[X]_S^2 \\ k_2[B] & k_3[X]_S^2 \end{pmatrix}. \qquad (26)$$

The matrix β^{-1} is the same as in (18) with $[X]_S$ and $[Y]_S$ from (25).

Kinetic coefficients (6) will be

$$\gamma = \frac{[X]_S}{N_A V} \begin{pmatrix} k_4 - k_2\,[B] & -k_2\,[B] \\ k_2\,[B] & k_2\,[B] \end{pmatrix}. \qquad (27)$$

Here we see the same situation as expressed by (20) and (21).

It is shown by Schnakenberg that for exhibiting a limit cycle behavior, a two-component chemical reaction system has to involve at least three reactions among which one must be autocatalytic [19]. The result is quite a lot of limit cycle systems, which are altogether simpler than the Brusselator with its number of four reactions.

For all oscillators, the oddness of the mutual correlation functions (20) and different signs of the kinetic coefficients (21) should hold, which follows directly from the oscillatory equation. The matrix of kinetic coefficients for an oscillator always contains an asymmetric contribution. This means that conservative forces contribute to the kinetic coefficients. Indeed, let us represent, formula (19) for example, for the Lotka oscillator in the form

$$\gamma = \frac{k_0}{N_A V} \left[\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \right]. \qquad (28)$$

Only the symmetrical part of the matrix of kinetic coefficients gives the entropy production. The skew part does not change the entropy.

Formulas (20) and (21) are a consequence of the temporal symmetry of the oscillation equations for fluctuations which do not correlate with each other at the initial moment. They are valid for any oscillatory systems, both non-equilibrium and equilibrium. In particular, in [12] an example of the fulfillment of these relations for thermal fluctuations of an equilibrium oscillator is given. In the equilibrium case, the variables in two-time correlation functions have different parity, and the explanation based on the principle of microscopic reversibility looks convincing. At the same time, this persuasiveness disappears for non-equilibrium steady states when two-time correlation functions of fluctuation quantities are calculated.

V. CONCLUSION

The above examples of chemical oscillators in OCSS confirm the made earlier, conclusion for OHSS that the Onsager–Casimir reciprocal relations hold only in equilibrium and are explained by the absence of stationary fluxes. In non-equilibrium steady states, the reciprocal relations turn out to be more complex than the Onsager–Casimir ones.

To construct non-equilibrium thermodynamics, Onsager's regressive hypothesis and the hypothesis of local equilibrium are sufficient. The kinetic coefficients must be determined on the basis of these hypotheses without any symmetry restrictions.

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СПІВВІДНОШЕННЯ ВЗАЄМНОСТІ ДЛЯ ХІМІЧНИХ ОСЦИЛЯТОРІВ

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Висунену раніше ідею про те, що для теплових гідродинамічних флуктуацій у відкритих гідродинамічних стаціонарних системах (ВГСС) співвідношення взаємності й загалом поведінка флуктуацій визначаються не принципом мікроскопічної зворотності, а наявністю або відсутністю потоку, застосовано до відкритих хімічних стаціонарних систем (ВХСС), де можуть відбуватися коливання концентрації реаґентів. Для таких хімічних осциляторів розглянуто поведінку концентраційних флуктуацій на фоні однорідних значень концентрацій реаґентів, тобто тоді, коли ще не виникли умови для макроскопічних коливань. Знайдені кінетичні коефіцієнти та співвідношення взаємності для хімічних осциляторів відмінні від співвідношення взаємності Онзаґера–Казимира. Показано, що вони мають загальний характер для різних моделей осциляторів. Підкреслено, що співвідношення взаємності Онзаґера–Казимира виконуються тільки в умовах рівноваги й не виконуються в умовах нерівноваги у відкритих системах за наявності потоків. Хімічні осцилятори якраз є прикладом відкритих систем, де нерівновага зумовлена потоком речовини. Також наголошено, що нерівноважна термодинаміка має будуватися без будь-яких вимог симетрії кінетичних коефіцієнтів.

Ключові слова: відкриті гідродинамічні стаціонарні системи (ВГСС), відкриті хімічні стаціонарні системи (ВХСС), хімічні осцилятори, концентраційні флуктуації, співвідношення взаємності.