Linear nonequilibrium thermodynamics of periodic processes and chemical oscillations

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ABSTRACT Onsager's phenomenological equations successfully describe irreversible thermodynamic processes. They assume a symmetric coupling matrix between thermodynamic fluxes and forces. It is easily shown that the antisymmetric part of a coupling matrix does not contribute to dissipation. Therefore, entropy production is exclusively governed by the symmetric matrix even in the presence of antisymmetric terms. In this work we focus on the antisymmetric contributions which describe isentropic oscillations and well-defined equations of motion. The formalism contains variables that are equivalent to momenta, and coefficients that are analogous to an inertial mass. We apply this formalism to simple problems such as an oscillating piston and the oscillation in an electrical LC-circuit. We show that isentropic oscillations are possible even close to equilibrium in the linear limit and one does not require far-from equilibrium situations. One can extend this formalism to other pairs of variables, including chemical systems with oscillations. In isentropic thermodynamic systems all extensive and intensive variables including temperature can display oscillations reminiscent of adiabatic waves.

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1 Introduction

Oscillatory systems in classical physics are non-dissipative adiabatic processes. Let us consider a mass m coupled to two identical springs with an adiabatic compression modulus, K (Fig. 1A). After a dislocation of the mass away from the equilibrium position one finds positional oscillations of the mass. As a consequence of dissipation, the mass will approach the resting position x_0 (Fig. 1), which is at the minimum of the mechanical potential, V. One finds an analogous problem if one replaces the springs by two identical pistons containing an adiabatically shielded ideal gas (Fig. 1B). The two gas volumes are thermodynamic ensembles, and the resting position of the system is given by the maximum entropy of the total gas. Thus, the minimum of the potential, V, and the maximum of the entropy, S, are analogous. For the monoatomic ideal gas $T \cdot V^{2/3} =$const. and $T^{5/3} \cdot p^{-2/3} =$const., respectively. This allows for a calculation of the spring modulus K. During an oscillation in volume, the gas containers consequently also display oscillations in temperature, pressure and internal energy. Since the only difference of the two systems in panels A and B is the material of the springs, it is obvious that the temperature of the two springs in panel A will also oscillate, while the resting position is defined by the maximum entropy of the springs. It is in fact the nature of isentropic oscillations that temperature and internal energy (and all other intensive and extensive variables relevant for the equation of states) of subsystems will oscillate. A non-mechanical example is a capacitor coupled to a solenoid coil (Fig. 1C), which displays oscillations in the electrostatic field, the charges on the capacitor plates, and of the electrical current (and the magnetic field, respectively) - but also of the temperature of the dielectric between the capacitor plates. The latter phenomenon is called the 'electrocaloric effect'. It is usually small but can assume large values close to phase transitions of the dielectric (1–3). It is due to the reduction of entropy in the dielectric upon increase of an electrical field. The corresponding phenomena in mechanics is called the mechanocaloric effect.

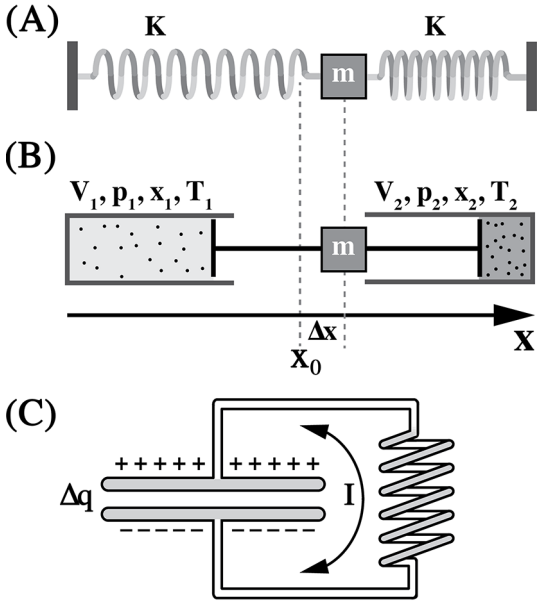

Figure 1: (A) Two springs with spring constant K attached to a mass m. (B) Two reservoirs 1 and 2 containing an ideal gas, which are coupled by a piston with mass m. (C) Oscillations of charge differences, Δq, and current, I, in a capacitance-inductor (LC) circuit.

A seemingly different class of oscillations has been found in some chemical reaction schemes such as the Belousov-Zhabotinsky (BZ) bromate reaction, the Briggs-Rauscher iodine clock or yeast populations under stress conditions. The BZ-reaction is a chemical clock containing $HBrO_2$, Br^-, Ce^{3+}/Ce^{4+}, or O_2 as intermediates which oscillate in time (4–6). Such reactions are thought to originate from far-from-equilibrium processes (7). Typically, one describes them as set of coupled non-linear rate equations containing autocatalytic intermediate products as free variables. They are exemplified by well-known reaction schemes such as the Brussela-

tor (7, 8) or the Oregonator (9). What such reaction schemes have in common is that temperature, pressure, the electrical potential and other thermodynamic variables that are not directly related to the concentrations, are not considered.
Interestingly, it is known that in some chemical systems such as the BZ-reaction the temperature oscillates in phase with the concentrations of the intermediates (Fig. 2 (A-C), (4, 10–12)). This is reminiscent of adiabatic oscillations such as the coupled pistons in Fig. 1. Similar oscillations in temperature or heat production rate have been reported in the Briggs-Rauscher reaction (13). There are also biological systems with similar responses, e.g. yeast cells (14) or the action potential in nerves (Fig.2 (D), (15, 16)), which may occur in periodic pulse trains. In the past, we have argued that the reversible changes in temperature found in nerves (Fig. 2 D) indicates that the nerve pulse is an adiabatic pulse reminiscent of sound rather than a dissipative wave (17, 18). The BZ-reaction shares similarities with the temperature response of nerves, i.e., it shares features of adiabatic processes.

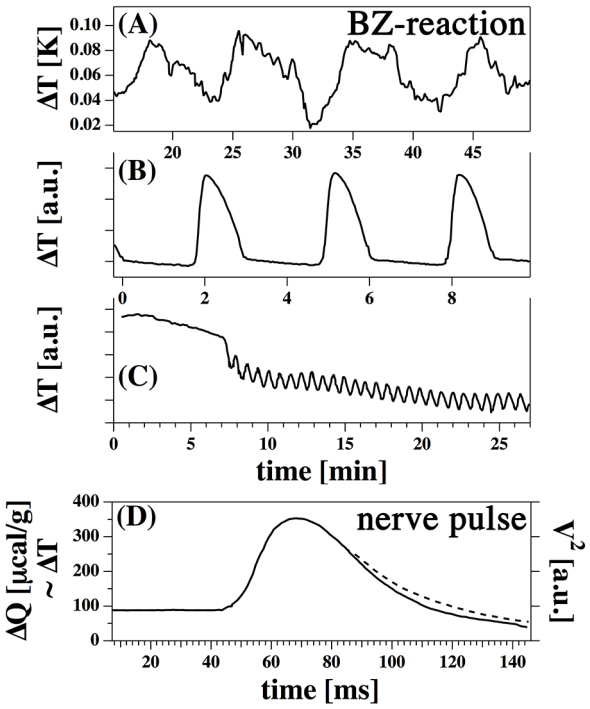

Figure 2: Temperature oscillations as a function of time in the Belousov-Zhabotinsky reaction and in nerves. (A) Adapted from (12) yielding up to 0.08 K in temperature variations. (B) Adapted from (4) and (C) Adapted from (10). (D) Heat transfer from a nerve into its environment, which is proportional to temperature changes, and the square of the voltage change V across the nerve membrane. Adapted from (16).

Linear nonequilibrium thermodynamics is applied to describe irreversible processes such as diffusion of particles and heat (e.g., (8, 19, 20)). The entropy is modeled as a harmonic potential (21). Far-from-equilbrium processes are thought being related to non-harmonic entropy potentials that could possess more than one entropy maximum with oscillations between them. In this article we explore the possibility that chemical oscillations and mechanical oscillations are both related to adiabatic processes, and that they can be described with the methods of linear non-equilibrium thermodynamics.

2 Theory

Making use of $dQ = TdS$, the first law of thermodynamics can be expressed as:

$$dS = \left(\frac{1}{T}\right) dE + \left(\frac{p}{T}\right) dV - \left(\frac{\Psi}{T}\right) dq ... - \sum_i \left(\frac{\mu_i}{T}\right) dn_i \ , \tag{1}$$

where dE, dV, dq, and dn_i are changes in extensive variables, while gradients of $1/T$, p/T, $-\Psi/T$ and $-\mu_i/T$ (or differences of these quantities between two reservoirs) are related to thermodynamic forces. Einstein proposed to treat the entropy as potential (21). In harmonic approximation, the entropy can be expanded around the equilibrium state as

$$S = S_0 + \frac{1}{2} \sum_{ij} \underbrace{\left(\frac{\partial^2 S}{\partial \xi_i \partial \xi_j}\right)_0}_{-g_{ij}} \xi_i \xi_j + ... \approx S_0 - \frac{1}{2} \sum_{ij} g_{ij} \xi_i \xi_j \ , \tag{2}$$

where the g_{ij} are the coefficients of a positive definite matrix with $g_{ij} = g_{ji}$ and $\det(\underline{\underline{g}}) > 0$ (all eigenvalues are positive). The variables are given by $\xi_i = (\alpha_i - \alpha_{0,i})$, where α_i is an extensive quantity (e.g., internal energy, volume, the number of particles of a particular species, charge, etc.), and $\alpha_{i,0}$ is the value of this variable in equilibrium. The consideration of the entropy as a potential led to the development of fluctuation-dissipation theorems pioneered by Greene and Callen (22, 23) and Kubo (24).

If a thermodynamic system is out of equilibrium, the system will relax back to more likely states and the entropy increases. Entropy production by a closed system evolving from a nonequilibrium state can be described by

$$\frac{dS}{dt} \equiv \sigma = \sum_i \underbrace{\frac{\partial S}{\partial \xi_i}}_{\equiv X_i} \underbrace{\frac{\partial \xi_i}{\partial t}}_{\equiv J_i} \equiv \sum_{ij} X_i J_i \ , \tag{3}$$

where the $X_i = \partial S / \partial \xi_i$ are the thermodynamic forces and the $J_i = \partial \xi_i / \partial t$ are the conjugated thermodynamic fluxes of the variables ξ_i.

Onsager (19, 20) expanded the fluxes as linear combinations of the forces, in analogy to Stokes law where the velocity of a body pulled in a viscous fluid is proportional to the drag force. According to Onsager, a thermodynamic system can then be described by a set of linear equations

$$\begin{aligned} J_1 &= L^S_{11} X_1 + L^S_{12} X_2 + ... \\ J_2 &= L^S_{21} X_1 + L^S_{22} X_2 + ... \\ J_3 &= ... \end{aligned} \tag{4}$$

or $\underline{J} = \underline{\underline{L}}^S \underline{X}$, where $\underline{\underline{L}}^S$ is a symmetric matrix. Eqs. (4) are called the 'phenomenological equations'. The formalism

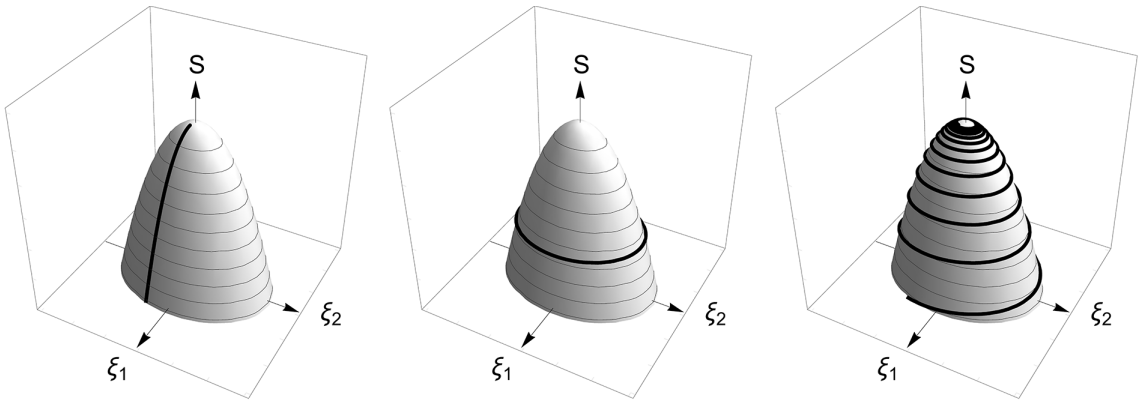

Figure 3: Schematic representation of dissipation, isentropic oscillations and real processes with both oscillations and dissipation in a harmonic entropy potential with two variables, ξ_1 and ξ_2.

is a natural extension of equilibrium thermodynamics. Taking into account Onsager's phenomenological equations, the entropy production of a nonequilibrium system in the linear limit is given by

$$\frac{dS}{dt} = \sum_{ij} L^S_{ij} X_i X_j = \sum_{ijkl} L^S_{ij} g_{jk} g_{il} \xi_k \xi_l \ , \qquad (5)$$

where in $X_i = -\sum_j g_{ij}\xi_j$ and $J_i = \sum L^S_{ij} X_j = -\sum_{jk} L^S_{ij} g_{jk} \xi_k$.

2.1 Dissipation

Onsager's decision not to consider the antisymmetric terms is based on the assumption that in a small sub-volume of a system thermal fluctuations do not display a preferred direction in time, i.e., that detailed balance is obeyed (20) and that fluctuations are Markovian. (There exist generalizations of Onsager's equations that include memory effects (25).) Onsager then assumed that a fluctuation and a macroscopic perturbation possess similar time evolutions. This is plausible for over-damped systems where inertial forces are small compared to the forces created by thermal fluctuations, and motion is dominated by random thermal collisions. However, one can imagine nonequilibrium states of thermodynamic systems prepared such that they display a preferred direction in time. The example in Fig. 1b is of this nature. In such systems, inertia is not generally small and Onsager's argument is not valid.

Any quadratic matrix $\underline{\underline{L}}$ can be written as a sum of a symmetric and an antisymmetric part, $\underline{\underline{L}} = \underline{\underline{L}}^S + \underline{\underline{L}}^A$, with

$$L^S_{ij} = \frac{L_{ij} + L_{ji}}{2} \qquad \text{and} \qquad L^A_{ij} = \frac{L_{ij} - L_{ji}}{2} \ . \qquad (6)$$

The matrix $\underline{\underline{L}}^A$ describes isentropic processes because it can easily be seen that

$$\sum_{ij} L^A_{ij} X_i X_j = 0 \ . \qquad (7)$$

It is therefore a natural consequence which does not require any further justification that only the symmetric matrix $\underline{\underline{L}}^S$ contributes to dissipation (shown in Fig. 3, left). Entropy production can more generally be written as $dS/dt = \sum_{ij} L_{ij} X_i X_j$ without making particular reference to the symmetry of the matrix $\underline{\underline{L}}$. As we will show, it is not generally justified to omit the antisymmetric terms. The terms associated to the antisymmetric matrix describe processes that conserve entropy (i.e., oscillations, shown in Fig. 3, center) while the combination of the two leads to damped oscillations as schematically described by Fig. 3 (right).

2.2 Oscillations

In the following we explore the implications of taking into account the antisymmetric terms only. We will consider simple oscillations in a harmonic entropy potential.

We assume systems with two variables, ξ_1 and ξ_2, with associated fluxes, J_1 and J_2, and two conjugated forces, X_1 and X_2. There is only one coefficient, L^A_{12}, and the phenomenological equations read

$$\begin{aligned} \frac{d\xi_1}{dt} \equiv J_1 &= L^A_{12} X_2 = -L^A_{12}(g_{21}\xi_1 + g_{22}\xi_2) \\ \frac{d\xi_2}{dt} \equiv J_2 &= -L^A_{12} X_1 = +L^A_{12}(g_{11}\xi_1 + g_{12}\xi_2) \ . \end{aligned} \qquad (8)$$

L^A_{12} may be positive or negative. The time derivatives of eq. (8) lead to

$$\begin{aligned} \frac{d^2\xi_1}{dt^2} &= -L^A_{12}\left(g_{12}\frac{d\xi_1}{dt} + g_{22}\frac{d\xi_2}{dt}\right) \stackrel{eq.8}{=} -\left(L^A_{12}\right)^2 \det(\underline{\underline{g}})\xi_1 \\ \frac{d^2\xi_2}{dt^2} &= +L^A_{12}\left(g_{11}\frac{d\xi_1}{dt} + g_{12}\frac{d\xi_2}{dt}\right) \stackrel{eq.8}{=} -\left(L^A_{12}\right)^2 \det(\underline{\underline{g}})\xi_2 \ , \end{aligned} \qquad (9)$$

which displays periodic solutions with $\xi_1 = \xi_{1,0} cos(\omega t + \phi_1)$ and $\xi_2 = \xi_{2,0} cos(\omega t + \phi_2)$ with a frequency, ω, given by

$\omega^2 = \left(L_{12}^A\right)^2 \det(\underline{\underline{g}})$. Thus, the antisymmetric part of the coupling matrix leads to oscillations.

The forces are linear functions of the fluxes of the extensive variables. Since the extensive variables oscillate, the conjugated thermodynamic forces also oscillate. This implies that in the isentropic case one also expects oscillations of the intensive variables such as temperature, pressure, electrical field and chemical potential.

2.3 Equations of motion for the isentropic case

The entropy is given by

$$S = S_0 - \frac{1}{2} g_{11}\xi_1^2 - g_{12}\xi_1\xi_2 - \frac{1}{2} g_{22}\xi_2^2 = \text{const.} \qquad (10)$$

By using eq. (8) we obtain for the two forces X_1 and X_2

$$\begin{aligned} \frac{\partial S}{\partial \xi_1} &= -g_{11}\xi_1 - g_{12}\xi_2 \quad \stackrel{eq.(8)}{=} \quad -\frac{1}{L_{12}^A}\,\dot{\xi}_2 \\ \frac{\partial S}{\partial \xi_2} &= -g_{12}\xi_1 - g_{22}\xi_2 \quad \stackrel{eq.(8)}{=} \quad +\frac{1}{L_{12}^A}\,\dot{\xi}_1 \ . \end{aligned} \qquad (11)$$

We will call eqs. (11) the thermodynamic equations of motion.

For an arbitrary even number of variables, we find that

$$\ddot{\underline{\xi}} = -\underline{\underline{L}}^A \cdot \underline{\underline{g}} \cdot \dot{\underline{\xi}} = \left(\underline{\underline{L}}^A \cdot \underline{\underline{g}}\right)^2 \cdot \underline{\xi} \qquad (12)$$

with oscillatory solutions. The thermodynamic equations of motion are given by

$$\underline{X} = \frac{\partial S}{\partial \underline{\xi}} = \left(\underline{\underline{L}}^A\right)^{-1} \dot{\underline{\xi}} \, . \qquad (13)$$

Simplification: For simplicity we assume in the following that $\underline{\underline{g}}$ is a diagonal matrix meaning that the principal axes of the entropy potential align with the variables under consideration. In the case of two forces and fluxes, eq. (8) yields

$$\xi_2 = -\frac{1}{L_{12}^A g_{22}} \frac{d\xi_1}{dt} \ . \qquad (14)$$

Therefore, the second variable is proportional to the temporal variation of the first variable, i.e., it is reminiscent of a momentum. Eq. (9) becomes

$$\frac{d^2\xi_1}{dt^2} = -\left(L_{12}^A\right)^2 (g_{11}g_{22})\xi_1 \qquad (15)$$

with oscillations of frequency $\omega^2 = \left(L_{12}^A\right)^2 (g_{11}g_{22})$. The thermodynamic equations of motion (eq. (11)) are given by

$$\begin{aligned} \frac{\partial S}{\partial \xi_1} &= -g_{11}\xi_1 \quad = \quad -\frac{1}{L_{12}^A}\dot{\xi}_2 \\ \frac{\partial S}{\partial \xi_2} &= -g_{22}\xi_2 \quad = \quad +\frac{1}{L_{12}^A}\dot{\xi}_1 \ . \end{aligned} \qquad (16)$$

Eqs. (11), (12) and (16) display a formal similarity to Hamilton's equations of motion, which for one spacial variable x with an associated momentum p are given by

$$\frac{\partial \mathcal{H}}{\partial x} = -\dot{p} \qquad \text{and} \qquad \frac{\partial \mathcal{H}}{\partial p} = +\dot{x} \, , \qquad (17)$$

where $\mathcal{H}$ is the Hamiltonian.

3 Examples

3.1 Oscillating piston (or spring)

Let us consider two coupled pistons with an associated mass, m, as given in Fig.1 (B). We assume that the position of the mass in equilibrium is given by x_0 and the deviation from equilibrium is Δx. Further, we assume that the pistons possess an adiabatic compression modulus K that can be calculated from the adiabatic equations of state of an ideal gas. (Two metal springs are conceptually equivalent but would possess different equations of state.)

The analytical mechanics description of this problem is

$$\mathcal{H} = \frac{1}{2} K\Delta x^2 + \frac{1}{2m} p^2 = \text{const.} \, , \qquad (18)$$

where $p = m\Delta\dot{x}$ is the momentum, and K is the compression modulus of the spring. Hamilton's equations of motion lead to

$$\frac{\partial \mathcal{H}}{\partial x} = K\Delta x = -m\Delta\ddot{x} \qquad (19)$$

$$\frac{\partial \mathcal{H}}{\partial p} = \frac{p}{m} = \Delta\dot{x} \, . \qquad (20)$$

Eq. (19) is Newton's second law, while eq. (20) is the definition of the momentum. Eq. (19) leads to an oscillation with $\omega^2 = K/m$.

The thermodynamic treatment leads to an equivalent description, as will be shown below. Let us assume that there are two variables, $\xi_1 \equiv \Delta x$ and ξ_2, and that g_{ij} is a diagonal matrix.

From eq. (14) it follows that

$$\xi_2 = -\frac{1}{L_{12}^A g_{22}} \frac{d\Delta x}{dt} \, . \qquad (21)$$

Entropy conservation leads to

$$\Delta S = -\frac{1}{2} g_{11}\Delta x^2 - \frac{1}{2g_{22}(L_{12}^A)^2} \left(\frac{d\Delta x}{dt}\right)^2 = \text{const.} \qquad (22)$$

At the present stage, the thermodynamic formalism does not know anything about the existence of a piston/spring or an inertial mass. The constants in its formalism acquire a meaning by comparison with a known physical situation. In the case of an oscillating spring, we find by comparison with eq. (18) that $1/g_{22}(L_{12}^A)^2 \equiv m$ corresponds to the mass attached to the piston and $g_{11} \equiv K$ corresponds to the compression

modulus (spring constant) of the setup in Fig. 1 (A). Eq. (15) yields

$$\frac{d^2(\Delta x)}{dt^2} = -\left(L_{12}^A\right)^2 (g_{11}g_{22})\,\Delta x\ . \tag{23}$$

Thus, the oscillatory frequency is given by

$$\omega^2 = g_{11}g_{22}\left(L_{12}^A\right)^2 \equiv \frac{K}{m}\ . \tag{24}$$

The thermodynamic equations of motion as given in eqs. (16) yield

$$\begin{aligned} \frac{\partial S}{\partial \xi_1} &= -g_{11}\Delta x = +\frac{1}{(L_{12}^A)^2 g_{22}}\frac{d^2\Delta x}{dt^2} \qquad \text{and} \\ \frac{\partial S}{\partial \xi_2} &= -g_{22}\xi_2 = +\frac{1}{L_{12}^A}\frac{d\Delta x}{dt}\ . \end{aligned} \tag{25}$$

It follows that

$$\begin{aligned} -\,g_{11}\Delta x &= \frac{1}{\left(L_{12}^A\right)^2 g_{22}}\Delta\ddot{x} \qquad \text{or} \\ -K\Delta x &= m\Delta\ddot{x}\ . \end{aligned} \tag{26}$$

This is the thermodynamic analogy to Newton's second law.

The thermodynamic formalism is absolutely equivalent to the analytical mechanical description of the same problem as given in eq. (17). This may not be surprising since the mathematics in both cases is based on the assumption of a harmonic potential. However, the terms acquire a different meaning because in contrast to the mechanical potential the entropy potential is rooted in statistics.

3.2 LC circuit

The derivations in the previous paragraph are independent of the choice of the extensive thermodynamic variable. Let us now consider an electrical LC-circuit with a capacitor of capacitance C_m and a solenoid coil with the inductance L, as shown in Fig.1 (C).

Let us again consider two variables, ξ_1 and ξ_2. The first variable $\xi_1 \equiv \Delta q$ shall be defined by the difference of the charge on the two capacitor plates in an LC-cirquit, with the conjugated force $-\Psi_{el}/T$ containing the electrostatic potential Ψ_{el} and the temperature T. The second variable ξ_2 is given by

$$\xi_2 = -\frac{1}{L_{12}^A g_{22}}\frac{d\Delta q}{dt} = +\frac{1}{L_{12}^A g_{22}} I\ , \tag{27}$$

where $I = -d\Delta q/dt$ is an electrical current (the negative sign originates from the fact that the charges flow out of the capacitor).

The entropy is conserved

$$\Delta S = -\frac{1}{2}g_{11}\Delta q^2 - \frac{1}{2g_{22}(L_{12}^A)^2}I^2 = \text{const.} \tag{28}$$

The analogous equation in electromagnetism is

$$E = \frac{1}{2}\frac{\Delta q^2}{C_m} + \frac{1}{2}LI^2 = \text{const.}\ , \tag{29}$$

where C_m is the capacitance and L is the inductance of the coil. By comparison, we find that $C_m \equiv 1/g_{11}$ and $L \equiv 1/g_{22}(L_{12}^A)^2$. The first term in eq. (29) is the electric energy, while the second term is the magnetic energy. They correspond to the potential and the kinetic energy in the previous problem.

Eq. (15) yields

$$\frac{d^2(\Delta q)}{dt^2} = -\left(L_{12}^A\right)^2 (g_{11}g_{22})\,\Delta q \tag{30}$$

with oscillatory solutions with

$$\omega^2 = \left(L_{12}^A\right)^2 g_{11}g_{22} = \frac{1}{LC}\ . \tag{31}$$

The thermodynamic equations of motion as given in eqs. (11) yield

$$\begin{aligned} \frac{\partial S}{\partial \xi_1} &= +\frac{1}{(L_{12}^A)^2 g_{22}}\frac{d^2\Delta q}{dt^2} \qquad \text{and} \\ \frac{\partial S}{\partial \xi_2} &= +\frac{1}{L_{12}^A}\Delta\dot{q}\ . \end{aligned} \tag{32}$$

From eqs. (16) and (32), it follows that

$$\begin{aligned} -\,g_{11}\Delta q &= \frac{1}{\left(L_{12}^A\right)^2 g_{22}}\Delta\ddot{q} \qquad \text{or} \\ \frac{1}{C_m}\Delta q &= L\dot{I}\ . \end{aligned} \tag{33}$$

This equation could also be derived from Kirchhoff's loop rule. Eq. (33) is the electrical analogy to Newton's second law. $L\dot{I} = -L\ddot{q}$ is the equivalent of an inertial force, an L plays the role of a mass. Thus, the thermodynamic formalism is equivalent to the electrical description of the same problem.

3.3 Oscillating reactions

The previous section suggests that there exist equivalents of inertia also in systems that are not of mechanical nature. In the electromagnetic case, the inductance plays the role of an inertial mass. Eq. (1) suggests that any pair of an extensive variable and its conjugated intensive variable play a comparable role. It seems plausible to suggest that one obtains meaningful thermodynamic relations for any pair of variables.

In chemistry, the extensive variables of interest are the number of particles in a chemical reaction, n_i, or the reaction variable of a reaction, ζ. Let us consider a chemical reaction

$$\nu_{X_1}X_1 + \nu_{X_2}X_2 + ... \overset{\zeta}{\leftrightarrow} \nu_{Y_1}Y_1 + \nu_{Y_2}Y_2 + ...\ , \tag{34}$$

where the X_i and Y_i are chemical reagents, and the ν_i are the reaction stoichiometries. We assume that our first variable $\xi_1 = \zeta$ is the reaction variable with the conjugated force

A/T. Here, $A = -\left(\sum \nu_{Y_i}\mu_{Y_i} - \sum \nu_{X_i}\mu_{X_i}\right)$ is the affinity of the above reaction, where the μ_i are the chemical potentials of the reagents. The second variable ξ_2 is given by

$$\xi_2 = -\frac{1}{L_{12}^A g_{22}}\frac{d\zeta}{dt}\ , \tag{35}$$

where $(d\zeta/dt)$ is the flux in the chemical reaction.

The entropy is conserved

$$\Delta S = -\frac{1}{2}g_{11}\zeta^2 - \frac{1}{2g_{22}(L_{12}^A)^2}\left(\frac{d\zeta}{dt}\right)^2 = \text{const.}\ , \tag{36}$$

where $L_c \equiv 1/g_{22}(L_{12}^A)^2$ is a chemical inductance.

Eq. (15) yields

$$\frac{d^2(\zeta)}{dt^2} = -\left(L_{12}^A\right)^2 (g_{11}g_{22})\,\zeta \tag{37}$$

with oscillatory solutions with frequency

$$\omega^2 = \left(L_{12}^A\right)^2 g_{11}g_{22} \equiv \frac{g_{11}}{L_c}\ . \tag{38}$$

The thermodynamic equations of motion yield

$$\begin{aligned}\frac{\partial S}{\partial \xi_1} &= +\frac{1}{(L_{12}^A)^2 g_{22}}\ddot{\zeta} \qquad \text{and}\\ \frac{\partial S}{\partial \xi_2} &= +\frac{1}{L_{12}^A}\dot{\zeta}\ .\end{aligned} \tag{39}$$

From eqs. (16) and (39), it follows that

$$-\,g_{11}\zeta = L_c\ddot{\zeta}\ , \tag{40}$$

which is the chemical equivalent of Newton's second law.

In analogy to the arguments above, not only the chemical potentials will oscillate but also the temperature. The latter effect could be called a chemocaloric effect. Such a behavior was found in various chemical oscillations, most notably in the Belousov-Zhabotinski reaction as discussed in the introduction.

4 Discussion and conclusions

We have shown here that by a generalization of the methods of linear non-equilibrium thermodynamics one can understand some simple oscillatory processes in the language of thermodynamics. While our considerations are very straightforward and simple, they have (to our knowledge) not been made previously.

Phenomenological Onsager-type equations yield fluxes that can be written as $\underline{J} = \underline{\underline{L}}\,\underline{X}$, where $\underline{\underline{L}}$ is an arbitrary matrix that can be uniquely separated into a symmetric and an antisymmetric matrix, $\underline{\underline{L}}^S$ and $\underline{\underline{L}}^A$, respectively. The symmetric part leads to dissipation described by the standard methods of nonequilibrium thermodynamics (8) while the the antisymmetric part contains oscillatory processes that conserve entropy. Onsager's decision to focus on a symmetric coupling matrix (20) is justified in systems where motion is dominated by random thermal collisions, and inertia can be neglected. However, the example of a piston containing an ideal gas connected to a mass (Fig. 1) demonstrates that one can construct thermodynamic systems where these assumptions do not hold true.

In particular, one finds oscillations even close to equilibrium and does not require (nonlinear) far-from-equilibrium situations. For each extensive variable ξ_1 there is a variable $\xi_2 = -(1/L_{12}^A g_{22})\dot{\xi}_1$ that behaves like a momentum. The physical nature of the variables can only be determined by comparison with a specific physical situation. Lowering the entropy can involve a changes away from uniform spatial distributions, or it can originate from the alignment of the motion of the particles. The first case is equivalent to the loading of a spring, or the charging of a capacitor. The second case corresponds, e.g., to the collective directed motion of particles, or to an electrical current. With the present formalism, one can find analogies to the oscillation in a spring and the oscillations in an electrical LC element and find analogies to Newton's second law. In particular, one finds equivalents of the inertial mass. For instance, the mass associated to an oscillating spring is analogous to the inductance in a solenoid coil. Since the formalism is identical for each pair of extensive and intensive variables, we proposed that isentropic oscillations in chemical reactions can exist in the linear thermodynamic limit, and that such oscillations are connected to chemical inertia involving the existence of a chemical inductance. The thermodynamic forces in the above examples are $\Delta(1/T)$, $\Delta(p/T)$, $-\Delta(\Psi/T)$ and $\Delta(A/T)$. They are proportional to the extensive variables. Therefore, not only the extensive variables but also the intensive variables including the temperature fluctuate and oscillate. For this reason, the experimental finding of periodic temperature changes in chemical oscillations (4, 10–12)) but also the reversible temperature changes in nerve pulses (15, 16, 26) is interesting and meaningful. It hints at adiabatic contributions to these oscillations.

We derived equations for the thermodynamic forces which we called the 'thermodynamic equations of motion.' They are analogous to Hamilton's equations of motion. This result may not be surprising because the problems described here are based on (harmonic) potentials in both formalisms, and thus the mathematics is analogous. However, they acquire a different meaning because in contrast to the analytical potential, V, the entropy, S, is based on statistical considerations. In the Hamiltonian formalism, energy is constant, while in the thermodynamic formalism entropy is constant and the internal energy oscillates between different compartments of the system and is not constant. It seems plausible that the two formalisms are not only similar by chance. Liouville's theorem of statistical mechanics states that along the trajectories of a mechanical system the density of states in phase space is constant (27). This is another way of stating that entropy is conserved, which is just the assumption made here for isentropic processes.

The postulate made in this work is that any spontaneous thermodynamic process in a harmonic entropy potential is composed of dissipative parts leading to entropy production

and entropy conserving processes leading to oscillations. The thermodynamic formalism can be applied to any pair of variables, and also to linear combinations of forces. Thus, one obtains the possibility of describing chemical oscillations with a formalism reminiscent of analytical mechanics. Chemical oscillations have been described by sets of nonlinear equations such as the Brusselator or the Oregonator (7). These schemes lead to stable limit cycles that are not very dependent on the initial conditions provided that some forces are kept constant. In contrast, in the present linear formalism forces are not fixed and therefore no limit cycles are present. However, depending on the relative contributions of the L_{ij}^S and L_{ij}^A, the formalism can lead to purely dissipative behavior (real eigenvalues), and to bifurcations leading to dampened oscillations with a number of eigenfrequencies that depends on the dimension of the matrix $\underline{\underline{L}}$. In a future publication we will explore this in more detail.

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