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Perspective

Global non-equilibrium thermodynamics for steady states like never before

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Abstract – In this Perspective article, we introduce a new framework for the global non-equilibrium thermodynamics of stationary states. This theory uses the spatial distributions of temperature, density, velocity, and other variables in stationary states as its input. It outputs the global state parameters to describe the system's energy exchange with the environment. The number of state parameters is determined solely by the type of substance in the system and external potentials, regardless of the number of boundary conditions, fluxes within the system, or its specific geometry. The theory offers a second law of non-equilibrium thermodynamics for stationary states, predicting the direction of spontaneous processes between them. When all macroscopic fluxes reach zero, the theory reduces to equilibrium thermodynamics.

perspective

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Introduction. – The internal energy in equilibrium thermodynamics depends on a few global state parameters, each representing an independent way of energy change. For an ideal gas, these parameters are entropy (heat), volume (volumetric work), and particle number (matter exchange). The number of such parameters must be determined through experiments and calculations, as no theory predicts them, especially in non-equilibrium states. Non-equilibrium states are typically non-uniform, sustaining energy fluxes through temperature, pressure, or concentration gradients, which locally define the system's state. Key questions arise: Can non-equilibrium stationary states be described using global parameters independent of spatial coordinates (fig. 1)? Can non-uniform states be mapped onto uniform ones to identify global energy exchange modes? Can the first and second laws of thermodynamics apply to steady states as in equilibrium? So far, research has been limited to systems close to equilibrium with minor temperature gradients [1–10]. Here, we extend the theory beyond near-equilibrium constraints.

Current description of non-equilibrium states. – The system is in a non-equilibrium state when a macroscopic energy flux (in any form) flows across the system.

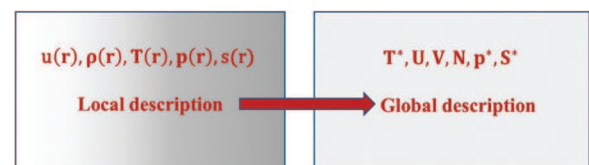


Fig. 1: The local description of stationary states is based on the energy density $u(\mathbf{r})$, density $\rho(\mathbf{r})$, temperature $T(\mathbf{r})$, etc. where \mathbf{r} is the position vector. By mapping the non-uniform system onto the uniform one, we change this local description into the global description in terms of a few global state parameters.

The most successful theory that explains how thermodynamic systems sustain the fluxes and how energy flows across them is called thermodynamics of irreversible processes or irreversible thermodynamics [11]. Three conservation laws of mass, momentum, and energy supplemented with local equations of state taken from the equilibrium thermodynamics and linear relations between thermodynamic fluxes and thermodynamic forces form the theory's core. The irreversible thermodynamics outputs the spatial and temporal distribution of density, velocity, temperature, pressure, etc., in the non-equilibrium state. These functions follow deterministic trajectories and end up either in equilibrium states when the fluxes go to zero or in stationary states when the fluxes go to a constant

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value sustained by external conditions. Some solutions of irreversible thermodynamics do not reach a stationary state but change continuously in time (*e.g.*, oscillatory reactions or turbulent states), even without time-dependent external forces. Extended irreversible thermodynamics goes beyond the local equations of state and linear flux-force relations. This theory introduces fluxes as additional thermodynamic variables (apart from those known from the equilibrium thermodynamics) [12]. One problem in extended models is the construction of equations describing the fluxes. Another route to the local description of non-equilibrium states is the stochastic thermodynamics [13] and macroscopic stochastic thermodynamics [14]. Stochastic thermodynamics is based on stochastic processes and the Master equation. The fluctuation theorems like Jarzynski's formula [15,16] and its extensions like Crooks [17,18] formula gave further insight into the experimental study of an ensemble of possible trajectories joining two equilibrium [19] or steady states [20]. In equilibrium, statistical mechanics and thermodynamics are intricately bound. Microscopic and macroscopic descriptions of matter out of equilibrium of similar duality [21,22] are yet to be discovered.

Another approach to non-equilibrium thermodynamics focuses on steady (stationary) states and the transition between them [1,23–25]. This approach aims to abandon the local equilibrium hypothesis and introduce the local steady-state hypothesis. In all these previous approaches, the system's state, either in the steady state or in the transition between the states, was described by parameters that varied in space and were thus local, according to our nomenclature.

The local description of non-equilibrium states is given by the quantities depending on the spatial variable \mathbf{r} and time, t : *e.g.*, velocity $\mathbf{v}(\mathbf{r}, t)$, number density $n(\mathbf{r}, t)$, temperature $T(\mathbf{r}, t)$. The equations of irreversible thermodynamics are the evolution equations for these quantities. The local description represents the internal energy density by $u(\mathbf{r}, t)$. We assume that the system is locally at quasi-equilibrium and satisfies the equations of state known from equilibrium thermodynamics, *e.g.*, for the ideal gas $u(\mathbf{r}, t) = 3/2 k_B n(\mathbf{r}, t) T(\mathbf{r}, t)$. In principle, the boundary conditions set the number of global independent variables needed to describe the energy change because all these distributions depend on the boundary conditions. On the contrary, the description of energy exchange with the environment in equilibrium thermodynamics is global. Irrespectively of boundary conditions or processes joining two equilibrium states, the internal energy $U(S, V, N)$ of the ideal gas is a function of only three global parameters (entropy S , volume V , and number of particles N) characterizing the system and its energy exchange with the environment. These global parameters are called state parameters. In this Perspective, we will show how to build a robust, global description of stationary non-equilibrium states in the same spirit as in equilibrium thermodynamics.

One important element missing in non-equilibrium thermodynamics is the variational principle, similar to the one known from equilibrium thermodynamics (the second law). The minimum entropy production [26–28], maximum entropy production [29,30], second entropy variations [31], or minimum energy dissipation [32] have never reached the same generality as the second law of thermodynamics for equilibrium states. The minimization of entropy production or energy dissipation resembles the minimization of the Lagrangian function known from classical mechanics. When we minimize the entropy production, a functional of density, temperature, concentration, etc., we get the equations of irreversible thermodynamics in the steady (stationary) states. Similarly, the minimization of a Lagrangian leads to Hamiltonian equations of motion. Researchers in non-equilibrium thermodynamics either want to retrieve the equations of motion from the variational principle or show that a given physical quantity continuously grows or decreases as the system approaches the equilibrium or stationary state. The extremum principle in equilibrium thermodynamics differs from the aforementioned ones because we compare the equilibrium state to some possible states obtained by imposing constraints on the system. We answer the following question: which of all states obtained by various constraints is the most stable according to the second law? The second law in the energy language is as follows. The internal energy $U(S, V, N, x)$ at constant S, V, N is minimized as a function of x at the equilibrium state, where x is the variable describing constraints in the system. Equivalently to the minimum energy principle, we state that the entropy $S(U, V, N, x)$ has a maximum as a function of x for constant U, V, N [33]. This article presents the first and second laws for non-equilibrium steady states using the same methodology as that used in equilibrium thermodynamics.

Ideal gas in a heat flow. – Here, we show the exact result for the stationary states of the ideal gas in the heat flow, leading to global state parameters for this simplest non-equilibrium system. We investigate the energy change between non-equilibrium steady states to extend thermodynamics' first law beyond equilibrium. We assume that the system has energy mass density, $e(\mathbf{r}, t)$, and energy flux density, $\mathbf{J}_e(\mathbf{r}, t)$, which satisfies the continuity equation

$$\partial_t \rho e = -\nabla \cdot \mathbf{J}_e, \quad (1)$$

with mass density $\rho(\mathbf{r}, t)$ [11]. The flux \mathbf{J}_e contains all possible ways of how the energy flows everywhere in the system,

$$\mathbf{J}_e = \rho e \mathbf{v} + P \cdot \mathbf{v} + \mathbf{J}_q, \quad (2)$$

with convection term $\rho e \mathbf{v}$ and fluxes of the energy due to mechanical work and heat. Here $\mathbf{v}(\mathbf{r}, t)$ is the velocity field, $P(\mathbf{r}, t)$ is the pressure tensor, $\mathbf{J}_q(\mathbf{r}, t)$ is the heat flux density.

We assume that the system starts evolving in time t_i toward another infinitesimally close steady state that is

reached in time t_f . The evolution of the system's surface, $\partial V(t)$, during the transition is also considered if needed. The above assumption allows us to determine the evolution of energy stored at the system's volume, $E(t) \equiv \int_{V(t)} d^3r \rho(\mathbf{r}, t) e(\mathbf{r}, t)$ in terms of fluxes. Because both states (final and initial) are infinitesimally close, we define the differential by $dE = E(t_f) - E(t_i)$ and with the use of the above assumptions, we obtain [34],

$$dE = - \int_{t_i}^{t_f} dt \int_{\partial V(t)} d^2r \hat{n} \cdot \mathbf{J}_e(\mathbf{r}, t). \quad (3)$$

The following integral gives the exchange of the total energy. As the total flux has three contributions, convective, mechanical work, and heat, they determine the division of how energy can be exchanged with the environment. For closed systems, the convective term vanishes [34], and the energy may change solely due to heat and mechanical work,

$$dU = dQ + dW, \quad (4)$$

where the heat differential is given by

$$dQ = - \int_{t_i}^{t_f} dt \int_{\partial V} d^2r \hat{n} \cdot \mathbf{J}_q(t), \quad (5)$$

and work differential by

$$dW = - \int_{t_i}^{t_f} dt \int_{\partial V(t)} d^2r \hat{n} \cdot P \cdot \mathbf{v}, \quad (6)$$

If there is no macroscopic motion in a given steady state, the kinetic energy of the system does not change, so a change in the total energy is the same as the change of the internal energy,

$$dU = dE. \quad (7)$$

Here U denotes internal energy of the system, $U(t) = E(t) - \int_{V(t)} d^3r \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)^2/2$. Moreover, with the local equilibrium assumption in the limit of slow transitions (*e.g.*, slowly compressing the system), the dominant part of the pressure tensor comes from the thermodynamic pressure, $P \approx p(z)$. In the heat flow the local pressure is constant $p(z) = p^* = 2U/3V$ and eq. (6) reduces to the work due to the compression of the system

$$dW = -pdV. \quad (8)$$

As in equilibrium thermodynamics, the above term has a straightforward generalization to non-uniform systems in gravity field [35].

There is no formal difference between equilibrium and steady state's energy balance. It is valid for closed systems with steady heat flow and without macroscopic motion. Due to the minimal number of assumptions, the presented first law is also valid for mixtures and systems that undergo steady chemical reactions, as long as the total energy flux has the form given by eq. (2). In the heat flow,

we found the exact result for the net heat that changes internal energy [34]: $dQ = T^* dS^*$, where $T^* = \frac{2U}{3Nk_B}$ and

$$\frac{S^*(U, V, N)}{Nk_B} = \left\{ \frac{5}{2} + \frac{3}{2} \log \left[\frac{2}{3} \frac{\varphi_0 U}{N} \left(\frac{V}{N} \right)^{2/3} \right] \right\}, \quad (9)$$

where φ_0 is a constant. Thus, the internal energy of ideal gas in a heat flow is described by three state parameters, $U(S^*, V, N)$: non-equilibrium entropy, S^* , volume V , and number of particles, N . S^* is only one part of the total entropy of the system [34],

$$S_{\text{tot}} \left(U, V, N, \frac{T_2}{T_1} \right) = S^*(U, V, N) + \Delta S \left(N, \frac{T_2}{T_1} \right) \quad (10)$$

(defined as the volume integral of a system with volume entropy density $s(z)$ [34]). The second part

$$\Delta S(N, T_2/T_1) = Nk_B \log \left[\left(\frac{T_2}{T_1} \right)^{5/4} \left(\frac{\log \frac{T_2}{T_1}}{\frac{T_2}{T_1} - 1} \right)^{5/2} \right] \quad (11)$$

is a function of the entropy production $\sigma = -A \int_0^L dz \kappa \nabla T(z) \cdot \nabla \frac{1}{T(z)} = \frac{A\kappa}{L} \left(\frac{T_2}{T_1} + \frac{T_1}{T_2} - 2 \right)$ [11]. It originates from the dissipative background sustaining the heat flux [26,27]. The difference between the total entropy and S^* vanishes because $\Delta S(U, A, L, T_2/T_1) \rightarrow 0$, when the system approaches the equilibrium state, $T_2/T_1 \rightarrow 1$. We underline that only S^* contributes to the net heat dQ . The entropy production, which enters through ΔS , does not affect the first law of non-equilibrium thermodynamics (4) at all.

Ideal gas in hydrodynamic flows. – We investigated the ideal gas's planar (steady and unsteady) compressible Poiseuille flows with a cylinder (see fig. 2) placed between the planes [36]. In the case of an unsteady flow in the system, the system's energy depends, in principle, on eight variables: time, inlet and outlet pressure, boundary temperature, two spatial coordinates of the cylinder, volume, and the number of particles. Here, we show numerically that exactly like in the quiescent case, $U(S^*, V, N)$ is a function of only 3 state parameters instead of seven parameters and time. We presented this numerical example to support the claim in the abstract about the number of state parameters.

For the steady flow, we analyzed three processes involving variations in pressure difference Δp between the inlet and outlet of the channel, wall temperature T_0 , and volume V . We varied only one parameter during each process while keeping the others constant. Our observations showed that the following relation holds in all cases:

$$dU = T^* dS^* - p^* dV + \mu^* dN. \quad (12)$$

Here $p^* = 2U/3V$, and $\mu^*(T^*, p^*)$ is the chemical potential of the ideal gas at temperature T^* and pressure p^* . This result confirms that the internal energy is a function of

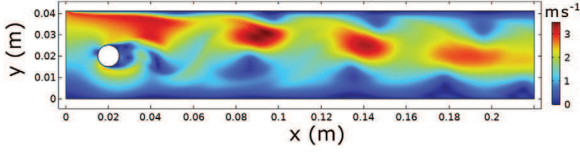


Fig. 2: Velocity profile in a planar Poiseuille flow with an asymmetrically positioned circular obstacle. The flow oscillates at increased Δp , and characteristic von Kármán vortices appear.

the three state variables S^* , V , and N in the case of the flow of matter across the system and heat flow through the walls. As an extension, we introduced a circular obstacle in the channel at position \mathbf{r}_c . At low values of Δp , the flow remains steady, and U depends on the obstacle's location through the state variables $S^*(\mathbf{r}_c)$, V , and $N(\mathbf{r}_c)$. When the pressure is increased (and the obstacle is positioned asymmetrically), the flow becomes oscillatory, displaying von Kármán vortices in the velocity profile (see fig. 2). In such oscillatory flows, we demonstrated that the internal energy depends on time via the state variables S^* and N , and is described as $U(S^*(t), V, N(t))$.

Global state parameters and the mapping procedure for interacting systems and external potential. – Here, we will show how to construct the state's parameters using a mapping procedure, *i.e.*, mapping a non-uniform system onto the uniform one (fig. 1) [35]. The mapping procedure works as follows: We average the distribution of pressure and total thermal energy over the system volume and set the global equations of state in the same form as in equilibrium. The global parameters of the state emerge according to this procedure. We use the following general equations: $U/V = \langle u(\mathbf{r}) \rangle$, $p^* = \langle p(\mathbf{r}) \rangle$, $N/V = \langle n(\mathbf{r}) \rangle$, where $\langle \cdot \rangle$ is the average over the volume, $u(\mathbf{r})$ is the energy per unit volume and $n(\mathbf{r})$ is the local number density. In all systems studied the global temperature $T^* = \langle n(\mathbf{r})T(\mathbf{r}) \rangle / \langle n(\mathbf{r}) \rangle$.

We consider the ideal gas, van der Waals gas, and the ideal gas in the gravitational potential confined between two parallel walls positioned at $z = 0$ and $z = L$ and maintained at different temperatures T_0 and T_L . For the ideal gas, we get

$$p = \frac{1}{L} \int_0^L n(z) k_B T(z) dz = \frac{N k_B T^*}{V}, \quad (13a)$$

$$U = \frac{3}{2} A \int_0^L n(z) k_B T(z) dz = \frac{3}{2} N k_B T^*. \quad (13b)$$

These equations define T^* . The global equations of state on the right-hand side of eq. (13a) have the same functional form as in the equilibrium state and thus naturally reduce to equilibrium equations of state in the limit of zero fluxes and uniform state. The pressure is uniform in the system, thus $p = p^*$. The mapping procedure gives the same formal structure as we know from equilibrium. Therefore, there is a variable S^* conjugated to T^* , which

is the non-equilibrium steady state entropy, eq. (9). It has the same form as at equilibrium but with T replaced by T^* . The internal energy of a non-equilibrium steady state is thus a function of three parameters of state $U(S^*, V, N)$ obeying relations

$$\left(\frac{\partial S^*}{\partial U} \right)_{V,N} = \frac{1}{T^*}, \quad \left(\frac{\partial S^*}{\partial V} \right)_{U,N} = \frac{p}{T^*}. \quad (14)$$

The mapping is straightforward also in the van der Waals gas, a system of interacting particles. We integrate local equations of state and find two new state parameters, a^* and b^* [35]:

$$U = \frac{3}{2} N k_B T^* - \frac{a^* N^2}{V}, \quad (15a)$$

$$p = \frac{N k_B T^*}{V} - \frac{a^* N^2}{V^2} + \frac{N k_B T^*}{V} \frac{N b^*}{V - N b^*}. \quad (15b)$$

In addition to the effective temperature T^* defined by the same expression as for ideal gases, these new state parameters are given by

$$a^* = a \frac{V^2}{N^2} \frac{1}{L} \int_0^L dz n(z)^2, \quad (16)$$

$$\frac{N k_B T^*}{V} \frac{N b^*}{V - N b^*} = \frac{1}{L} \int_0^L \frac{n(z) k_B T(z)}{1 - b n(z)} dz - \frac{N k_B T^*}{V}.$$

The internal energy of the van der Waals gas in the non-equilibrium steady state is thus a function of five parameters of state $U(S^*, V, N, a^*, b^*)$. Now the form of heat in the expression for the first law of non-equilibrium steady-state thermodynamics, dQ , acquires additional terms

$$dQ = T^* dS^* - \frac{N^2}{V} da^* + n k_B T^* \left(\frac{V}{N} - b^* \right)^{-1} db^*. \quad (17)$$

The state parameters a^* and b^* appear in the net heat differential because, in a non-uniform system, the change in the density profile leads to the local absorption or release of heat affecting in this way the net heat.

Global non-equilibrium thermodynamics also describes the thermodynamic system in the presence of external potential. Consider a column of height $L = z_L - z_0$ with base area A filled with perfect gas (of molar mass M) placed in a gravitational field with acceleration $-g\hat{\mathbf{e}}_z$. We will assume that the bottom of the column is immobile. This restriction can be released, leading to one more state parameter [37]. The mapping procedure allows the calculation of the total energy in the system, being the sum of already known thermal energy and potential energy,

$$U = \frac{3}{2} N k_B T^* + \frac{N M^* g L}{2}, \quad (18)$$

where the additional state parameter M^* is defined as the integral of gravitational potential energy over the system's volume,

$$\frac{N M^* g L}{2} = A \int_{z_0}^{z_L} M n(z) g (z - z_0) dz. \quad (19)$$

The external potential introduces anisotropy in pressure. To change the surface area of the base, one has to overcome the average pressure inside the column,

$$p^* = \frac{Nk_B T^*}{V}, \quad (20)$$

while compressing the column requires

$$p = \frac{Nk_B T^*}{V} - \frac{NM^* gL}{2V}. \quad (21)$$

As a consequence, the energy differential (4) includes heat

$$\delta Q = T^* dS^* + N \frac{gL}{2} dM^*, \quad (22a)$$

and work

$$\delta W = - \left(\frac{Nk_B T^*}{V} - \frac{NM^* gL}{2V} \right) A dL - \frac{Nk_B T^*}{V} L dA. \quad (22b)$$

The new parameter of state M^* is due to the shift of the center of mass in the temperature gradient. The mapping procedure is straightforward for the van der Waals gas in the presence of gravity [37].

Summarizing: if material parameters exist in the equations of state like a or b for the van der Waals gas, they will all become state parameters in stationary states. For example, in the binary ideal gas mixtures, we get a renormalized number of degrees of freedom, f^* , as the state parameter [38]. In the system of dipoles subjected to an electric field or magnetic material in the magnetic field, we expect that electric and magnetic susceptibility will become state parameters.

The second law of non-equilibrium thermodynamics: direction of spontaneous processes. – In our previous sections, we showed that the formal structure of the first law of the global non-equilibrium thermodynamics is the same as in the equilibrium thermodynamics. Here, we postulate that the second law for our thermodynamical description of stationary states also has the same structure as the one in equilibrium thermodynamics [37]. For systems that interact only thermally with the environment, the minimization principle says that $dF = dU - \delta Q \leq 0$, where δQ is the infinitesimal heat exchanged with the environment when the system goes from a less stable state to the equilibrium state. Therefore, we expect that in stationary states, the minimization (fixed boundary conditions) follows the inequality

$$dU - \delta Q \leq 0 \quad (23a)$$

if we move from a less stable to a more stable steady state. When the system exchanges heat and work, δW , in any form with the environment, the second law should satisfy the inequality

$$dU - \delta Q - \delta W \leq 0 \quad (23b)$$

in non-equilibrium and equilibrium thermodynamics. How should we understand this law? In equilibrium

thermodynamics, we use the notion of constraints. The free energy $F(T, V, N, x)$ has a minimum at equilibrium state as a function of x at constant T, V, N , where x denotes a constraint, *e.g.*, a location of the movable internal wall in the system [37]. An external device changes x and moves the system between states inaccessible by changing T, V, N alone. This external device performs work δW_z . The first law of thermodynamics states that $dU = \delta Q + \delta W_z$. Now $dU - \delta Q \leq 0$ means that $\delta W_z \leq 0$. In short, if we move from a less stable state to a more stable state via the equilibrium/stationary states, the system does work on the external device. This law sets the directions of spontaneous processes between equilibrium and also between stationary states. Generally, a finite path in parameter space can connect non-equilibrium steady states. Thus, we must calculate the external work done along the path $W_z = \int (dU - \delta Q) \leq 0$. Along the path, all control and boundary conditions are constant [37]. Additionally, $dU - \delta Q$ is the exact differential along this chosen path in the space of state parameters. The extension of the second law to stationary states is a postulate, but it has been tested in systems with movable and permeable walls [37]. In the next section, we show its application to chemical reactions.

Non-equilibrium chemical systems: global stability of steady states derived from the second law of non-equilibrium thermodynamics. – Multiple steady states frequently occur in chemical reactors because the heat generated during reactions changes nonlinearly with temperature. The key question is: which of these states is the most stable under fixed reactor conditions? Despite more than 100 years of research into out-of-equilibrium chemical reactions, this question remains unanswered and is addressed in this section. Here we apply the second law of non-equilibrium thermodynamics described in the preceding section.

We consider an ideally mixed (usual assumption in chemistry) mixture of NO_2 and N_2O_4 in a photoreactor illuminated with a laser. Only NO_2 interacts with the light, absorbing visible light energy and dissipating it into heat [39]. The system has a uniform temperature $T = T^*$ different from the temperature of the thermostat T_e . Thus, there is a continuous heat flux from the system to the thermostat. A simple reaction of dimerization occurs $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$. First, we determine the stationary states of the system from the energy balance and chemical equilibrium.

Fulfilling the energy balance condition means that the energy absorbed from the laser beam by NO_2 must equal the heat exchanged with the thermostat. We assume that absorption is proportional to light intensity I_0 and NO_2 concentration n_2 , whereas heat exchange is proportional to the temperature difference between the system T and the thermostat T_e . Hence, the energy balance equation has the form

$$\alpha I_0 n_2 = \beta (T - T_e). \quad (24)$$

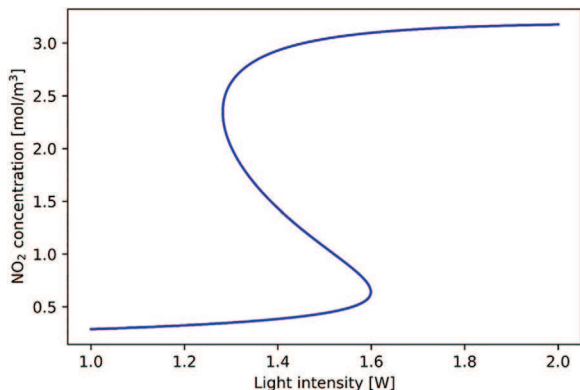


Fig. 3: Stationary states of the photoreactor for fixed cooling temperature. For a range of light intensities, there are three stationary states. The lower branch is called the low-temperature state, and the upper one is the high-temperature state. The middle one is locally unstable.

Moreover, chemical equilibrium conditions $K_c(T) = \frac{n_2^2}{n_1}$ must hold, where $K_c(T)$ is the equilibrium constant and n_1 , n_2 are concentrations of N_2O_4 and NO_2 , respectively. They satisfy the relation $n_1 = n_0 - \frac{1}{2}n_2$, where n_0 is the constant reflecting the fixed amount of matter in the reactor. If we fix the so-called control parameters (I_0, T_e), we have a system of non-linear equations solved for T and n_2 . These equations may have many solutions for a range of control parameters corresponding to multiple stationary states. Figure 3 presents an example of this phenomenon. The generalized second law of thermodynamics determines the globally stable state. Elementary change of the internal energy is

$$dU = dQ + \mu_1 dN_1 + \mu_2 dN_2. \quad (25)$$

The heat dQ is the energy absorbed from the laser beam, and the rest is associated with the chemical reaction. Hence, the second law has the form

$$\mu_1 dN_1 + \mu_2 dN_2 \leq 0. \quad (26)$$

We must integrate the above differential form on a path joining the states to determine work W_z done between two stationary states corresponding to the same control/boundary parameters. The path is a continuum of stationary states. The energy balance equation holds along it, and the system's temperature on this path must be tuned to NO_2 concentration. Well-known formulae for the chemical potential of ideal gas give conditions for the relative stability of two stationary states:

$$W_z = \frac{1}{2}V \int_{n_2^p}^{n_2^k} \left(\Delta_r G^\circ(T(n_2)) + RT(n_2) \log \left(\frac{RT(n_2)}{p_0} \cdot \frac{n_2^2}{n_0 - \frac{1}{2}n_2} \right) \right) dn_2 \leq 0, \quad (27)$$

where $\Delta_r G^\circ$ is the standard reaction Gibbs energy and $p_0 = 10^5$ Pa. Function $T(n_2)$ is given by condition (24).

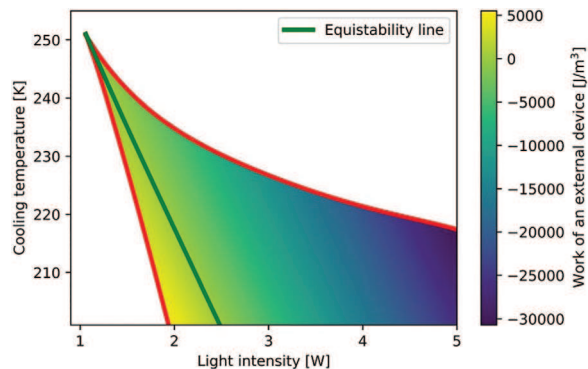


Fig. 4: Work of an external device associated with changing the system's state from low to high temperature for given control parameters (cooling temperature and light intensity).

The integral can be evaluated for a range of control parameters I_0 , T_e . The results are presented in fig. 4. The green line is the so-called equi-stability line. For control parameters on this line, integral (27) is zero, so the external device does not perform work to change the system's state. The cold state is more stable on the left of the line (for low light intensity). The same condition, eq. (27), was derived by Ross [40] using thermodynamics and stochastic processes. He called the function obtained from eq. (27) a Lyapunov function for the system, $W_z(N_2) = \int (\mu_2 - \mu_1) dN_2$. This is the external work necessary to move the system from the initial state to some intermediate state (defined by the number of molecules N_2) along stationary states. We go further. Our preliminary results show that using the mapping procedure, we can handle the reactor's non-uniform temperature $T(\mathbf{r})$ and concentration, $n(\mathbf{r})$ and, moreover, extend the calculations to flow reactors. In the non-uniform reactor, we use T^* as the effective temperature. Finally, the second law allows us to define the Lyapunov function for thermodynamic non-equilibrium systems, and thus, our approach complements the one obtained within stochastic thermodynamics [41].

Summary and future directions. – Our non-equilibrium thermodynamics is pedagogically explained in a lecture delivered at the Dream Chemistry Award Competition [42].

The stationary states and equilibrium states do not depend on time. The energy fluxes are zero in equilibrium states. They are, thus, special cases of stationary states where fluxes are constant. Therefore, according to the general physics methodology, a single theory should coherently describe both states. The mapping procedure allows us to define state parameters and formulate the first and second laws for equilibrium and stationary states. Our global non-equilibrium thermodynamics applies to both types of states. Although we use irreversible thermodynamics to compute the state parameters and their changes as we move from one stationary state to the other, the

formalism does not depend on any specific equations that lead to the distribution of pressure, density, or temperature. In particular, our theory does not rely on the linearity of flux-force relations or the local equilibrium hypothesis, which imposes the local equations of state in the same way as equilibrium thermodynamics. If some new non-local equations of state are used in irreversible thermodynamics, our formalism will not change. We will only have to integrate the non-local equations of state over the system's volume and demand that global equations of state have the same form as in equilibrium thermodynamics. In this sense, our formalism is robust and works arbitrarily far from equilibrium. From theory or experiment, we only need density, temperature, and pressure distribution in space. What do we gain using the theory? First, we reduce the number of parameters describing energy exchange with the environment. Irrespectively of the number of boundary conditions, flow conditions, or geometry of the system, the ideal gas will always be described by only three state parameters, and the van der Waals gas by only five state parameters. Second, the theory predicts which locally stable stationary states (for fixed boundary conditions) are globally stable and where transitions occur, as we showed for the photoreactor. Finally, our global non-equilibrium thermodynamics reduces very simply to the equilibrium thermodynamics in zero flux limit. Our theory offers the same robustness for the physical systems in stationary states as equilibrium thermodynamics in equilibrium states. Moreover, the second law of global non-equilibrium thermodynamics allows us to calculate the Lyapunov functions for thermodynamic systems, enabling further usage in stochastic thermodynamics.

Data availability statement: All data that support the findings of this study are included within the article (and any supplementary files).

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