

Challenges in thermodynamics: Irreversible processes, nonextensive entropies, and systems without equilibrium states*

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Abstract: Recent works on evaporation and condensation demonstrate that even these simplest irreversible processes, studied for over 100 years, are not well understood. In the case of a liquid evaporating into its vapor, the liquid temperature is constant during evaporation and the evaporation flux is governed by the heat transfer from the hotter vapor into the colder liquid. Whether liquid evaporates into its own vapor or into the vacuum, the irreversible pathway in the process goes through a number of steps which quickly lead to the steady-state conditions with mechanical equilibrium in most parts of the system—the fact overlooked in all previous studies. Even less is known about general rules which govern systems far from equilibrium. Recently, it has been demonstrated that a work done in an irreversible process can be related to the free energy difference between equilibrium states joined by the process. Finally, a real challenge in thermodynamics is a description of living systems since they do not have equilibrium states, are nonextensive, (i.e., they cannot be divided into subsystems), and cannot be isolated. Thus, their proper description requires new paradigms in thermodynamics.

Keywords: condensation; evaporation; irreversible processes; Jarzynski equation; living matter; nonextensive; phase separation; Renyi, Tsallis entropies.

OPENING REMARKS

Irreversible pathways connecting two equilibrium states are not well understood. Even less is known about general rules which govern systems far from equilibrium. In this mini-review, I have made a choice of some problems which, in my opinion, define challenges facing our community of thermodynamics and statistical mechanics. Among them I will present the Jarzynski equation, discovered in 1997, which relates works done in irreversible processes to the free energy difference [1–5]. Furthermore, I will describe recent findings concerning dynamic pathways governing evaporation and condensation [6–19] and mention late stages of a process of phase separation [20]. I will also discuss systems that are nonextensive and therefore cannot be described by the Boltzmann–Gibbs–Shannon (BGS) entropy. In its place, new paradigms are introduced such as Renyi or Tsallis entropies [21–26]. Finally, I will briefly touch on the problem of systems, such as living matter, which by definition do not have equilibrium states. We cannot use, in their context, a paradigm of isolated system or equilibrium

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state or even a notion of subsystem. Most certainly, new descriptions and new paradigms are needed to properly describe such systems.

FREE ENERGY CHANGE VERSUS WORK DONE IN IRREVERSIBLE PROCESSES

Let us consider two equilibrium states A and B both at the same temperature. In classical thermodynamics, in order to determine the Helmholtz free energy difference between A and B we construct a reversible process between A and B. The work done in this process is equal to the free energy difference

$$W_{\text{irreversible}} = F_{\text{B}} - F_{\text{A}} = \Delta F \quad (1)$$

If $\Delta F \geq 0$, then out of all pathways (reversible and irreversible) connecting A and B, the work done along the reversible pathway is the smallest. As is commonly accepted in classical thermodynamics, along irreversible pathways we encounter dissipation of energy, i.e., part of the energy that could be used as work is dissipated as heat. Therefore, the work necessary to move a system from A to B (and increase its free energy) in the irreversible process is larger than in the reversible one

$$W_{\text{irreversible}} \geq W_{\text{reversible}} \quad (2)$$

From eq. 2, it follows that for any irreversible process

$$W_{\text{irreversible}} \geq \Delta F \quad (3)$$

The works of Boltzmann and Maxwell published at the end of the 19th century pointed out the statistical origin of the laws of thermodynamics. The statistical nature of these laws imposes averages instead of single values. In this context, eqs. 1–3 should be rewritten as

$$\langle W \rangle \geq \Delta F \quad (4)$$

where the average $\langle \dots \rangle$ is taken with respect to all pathways connecting A and B (including reversible pathways) and W is the work done along a pathway, irrespective of whether it is a reversible or irreversible one. The statistical nature of the law changes its interpretation a bit. In principle, we can have irreversible pathways along which work done is smaller than along reversible pathways, yet eq. 4 tells us that such pathways are rather rare. The inequality in eqs. 2–4 precluded deeper studies of the relation between free energy difference between two thermodynamic states and the irreversible process joining them until 1997. In the *Physical Review Letters* paper, Chris Jarzynski derived [1] the following equality relating work and free energy difference:

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F) \quad (5)$$

where $\beta = 1/k_{\text{B}}T$ is the Boltzmann factor. The work, W , done along all processes joining two equilibrium states, contains information about the free energy difference between these states. In principle, it means that by repeating the same experiment many times and taking the average in eq. 5 we can obtain the free energy. However, eq. 5 is not practical for macroscopic systems since the number of repeated experiments, necessary for a good statistics, would grow exponentially fast with the size of the system or more precisely with the amount of dissipated work divided by the characteristic thermal energy $k_{\text{B}}T$. Nevertheless, eq. 5 is a perfect tool for the study of small thermodynamic systems on a nanoscale. A prime example is the determination of the free energy difference of macromolecule stretched by external force (optical tweezers or atomic force microscopy tip) [4,5]. In this case, we determine the whole free energy landscape associated with the stretching process since the initial A and final state B in eq. 5 do not have to be equilibrium states. Equation 5 is also a perfect tool in computer simulations. In a standard approach, we have to simulate a path of equilibrium states. Using eq. 5, we can make many non-equilibrium simulations and yet determine the free energy difference as in the standard approach [1–5].

EVAPORATION PROCESS

The Jarzynski formula derived in 1997 was an unexpected and surprising result with far-reaching consequences. But even in some very old fields of irreversible thermodynamics, there is plenty to be discovered. For example, boiling and, in general, evaporation are observed by us every day. Yet this irreversible process is far from being understood. Basic equations that govern the process are known. Yet, rarely are these equations solved for processes in multiphase systems [6]. In order to solve hydrodynamic equations in such a system, we need huge grids, especially if the phases exhibit large density differences (as in the case of vapor and liquid) or concentration differences (as in the case of oil and water). The size of the interface is at most 1 nm, and the liquid/vapor density ratio in normal conditions is of the order of 1000. To correctly approximate density gradients in the system, the number of grid points per interface (per 1 nm) should be of the order of 1000. From this estimate, we find that a solution of hydrodynamic equations in a large system of 1-m size requires 10^{36} grid points in the 3D system. Therefore, solutions of hydrodynamic equations in the two-phase region during phase transitions are limited to the microscale only. Even if we solve these equations in each phase independently, ignore and try to match the solutions at the interface, we are still faced with the problem of boundary conditions at the interface. These conditions are crucial for the dynamics of the irreversible process. In the case of evaporation, the evaporation flux comes directly from the interface, thus, without apriori knowledge of the boundary conditions such solutions are likely to fail. Problems exist also in the implementation of molecular dynamics simulations to processes occurring in two-phase regions. The typical number of particles in the simulations rarely exceeds a million, and time-scales are rarely longer than 10 ns, thus, these studies are limited to the nanoscale only [7]. On the experimental side, one usually encounters problems with the determination of various thermodynamic quantities close to the interface. There are no standard measuring devices to monitor density, temperature, and pressure at the micrometer length scale. Thus, in most experiments one is not able to study in detail the profile of temperature, density, and pressure close to evaporating droplets [8]. That is why, despite more than 100 years of active study of evaporation phenomenon, our knowledge of the dynamic pathway of this phase transition is limited and largely based on speculations rather than on solid experimental facts or computer simulations.

The first theoretical description of evaporation was given by James Clerk Maxwell in 1879 [9]. He assumed that the rate of evaporation was controlled exclusively by the diffusion of molecules (mass diffusion) in a vapor. He neglected an energy balance equation and the pressure balance and assumed a stationary distribution of vapor density around evaporating droplets. He further assumed that neither heat transfer nor pressure distribution limit the process. His description assumed that the energy necessary to evaporate liquid is transported immediately to the evaporating liquid. Following the Maxwell paper, there were a great number of theories of evaporation which were developed and refined over the last 100 years. They were based on approximations that greatly underestimated the role of energy flux, owing to temperature gradients in the vapor phase, and energy balance during the evaporation process. In the seminal paper by Schrage [10] published in 1953 (more than 70 years after Maxwell) he concluded his article as follows: "It was shown that the gas temperature during an evaporation or condensation process is not necessarily identical with the temperature of a liquid or solid surface. This fact has not been generally recognized...". Even today the primary quantities of interest in the theoretical approach are the evaporation coefficient, condensation coefficient, accommodation coefficient, and the reflected flux of the vapor molecules, without a proper analysis of the temperature, density, and pressure distribution in the system [11–14]. A typical formula for evaporation, for a droplet of radius R , from classical theories of evaporation which followed the Maxwell approach is given by the following equation [15]:

$$R^2(t) - R^2(t = 0) = -2D_s \rho_s t / \rho_{\text{liq}} \ln[1 + c_p(T_{\text{vap}} - T_s) / \Delta H] \quad (6)$$

where D_s is the self-diffusion at the evaporating droplet surface, ρ_s is the surface density, T_s is the surface temperature, and T_{vap} is the vapor temperature; c_p is the vapor specific heat and is the evaporation enthalpy. The heat conductivity or the wall temperature does not appear in this formula, as if the heat transfer was instantaneous while the mass transfer in vapor was a limiting factor for evaporation. Moreover, the formula contains some ill-defined quantities such as $D_s\rho_s$; they can vary over three orders of magnitude across the interfacial width, ξ (of size of few molecular diameters), and, moreover, they have never been measured close to the interface or across a two-phase system. T_s can also vary across the interface. Moreover, the value of T_{vap} is not well defined, since the temperature has a profile inside the vapor phase. Simplicity of the evaporation law [$R^2(t) \sim t$] and lack of precise experiments precluded proper verification of the theories against experimental results.

In 1999, Fang and Ward [8] made very precise measurements of the temperature distribution close to the evaporating surface of water and found that the temperature is discontinuous at the interface, with the vapor temperature T_{vap} higher than the liquid temperature T_{liq} . This result contradicted the commonly accepted theories of evaporation based on the linearized Boltzmann equation in a vapor phase. The authors concluded their paper as follows: “at present there does not appear to be any explanation for this observation from classical mechanics. It remains to be seen if quantum mechanics will provide an explanation”. It is tempting to speculate at this point that theories of evaporation somehow had very little input from experimental studies during the last 100 years. Careful experiments by Fang and Ward [8] revealed the weakness of commonly accepted theories, which followed Maxwell’s original work. In 2004, Bond and Struchtrup [11] argued, using elements of kinetic theory of gases combined with elements of irreversible thermodynamics, that temperature discontinuity is strongly related to the energy flux during evaporation, a quantity grossly neglected in the theories of evaporation. They concluded that the temperature discontinuity found in experiments cannot be obtained from the classical Hertz–Knudsen or Schrage models of evaporation.

In the last three years, new results emerged from computer simulations and irreversible thermodynamics in a two-phase region, revealing many new phenomena which accompany evaporation [6,7,16] and condensation [17]. The solutions of hydrodynamic equations during evaporation and computer simulations revealed that mechanical equilibrium establishes very fast in the system (even if the system evaporates into the vacuum and extra pressure comes from the momentum flux accompanying evaporating molecules). It seems to be a rule that a dynamic pathway chosen by the system during evaporation is such as to quickly achieve (if possible) mechanical equilibrium. Temperature and density are slave variables which have to adjust their profiles to satisfy this equilibrium. Even in the case of evaporation into vapor, the momentum flux from the surface of the liquid is equal to the pressure inside a liquid.

In order to properly describe evaporation, one has to specify initial and boundary thermodynamic conditions during evaporation. If the evaporating liquid does not have a contact with a hot stage (i.e., heat flux comes exclusively from a surrounding vapor) density, chemical potential, and pressure are uniform inside a liquid. There are, however, differences between different geometries. Evaporating liquid droplets have constant temperature and density while inside evaporating films temperature continuously increases during evaporation, while density continuously decreases in time. The temperature and density have well-defined profiles inside a vapor phase which rather strongly depend on a distance from the evaporating surface, while pressure is constant. At the interface between the vapor and evaporating liquid, temperature is continuous only if the liquid/vapor density ratio is of the order of 10, i.e., only when evaporation occurs close to the critical point. At normal conditions, far from the critical point, the density ratio is large, approaching 1000, and in such cases we expect a temperature jump at the interface. Most probably, temperature jumps are related to the mechanical equilibrium in the system, which, as mentioned before, accompany evaporation.

If the evaporating liquid is continuously supplied with energy (e.g., by laser heating) or evaporates into the vacuum, when the kinetic energy of molecules is converted into the evaporation enthalpy, the density and temperature are no longer uniform inside a liquid. In the droplet, the density has a min-

imum in the center, while the temperature has a maximum at this point. Density increases and temperature decreases as a function of the distance from the droplet, yet pressure is constant inside the droplet. Mechanical equilibrium is established by the momentum flux of vapor molecules across the interface and together with the surface tension match the pressure inside a liquid.

Apart from the late stages of evaporation described above, which proceed in a quasi-stationary way, some interesting phenomena occur in the very early stages of evaporation, i.e., during the heating stage [6,7,18]. A sudden increase of temperature at the walls (here the time-scale of heating should be faster than the size of the container divided by the speed of sound) of a container, where there is a liquid droplet inside at equilibrium with its vapor, initiating sound waves which move from the boundary to the droplet surface. These waves heat up a droplet. The heating process is due to the condensation of hot vapor at a colder surface of the droplet, thus, paradoxically, evaporation starts with initial condensation of vapor. Owing to this condensation process, a droplet increases its temperature (even by 20 to 30 degrees in small systems) and size (by few percent). Interestingly, the final temperature of a droplet (a droplet has a constant temperature during later stages of evaporation) does not depend on the rate at which the walls are heated, provided that the final temperature at the walls is the same in each case.

Finally, the rate of change of the droplet radius $R(t)$ with time t which very well describes evaporation in a nano- and microscale (i.e., the formula was tested in molecular dynamics simulations and in the solutions of hydrodynamic equation, thus in a range of sizes smaller than 1 μm) is as follows [6,7]:

$$R(t)^2 - R(t=0)^2 = -2\kappa_{\text{vap}}(T_{\text{b}} - T_{\text{s}})/(\rho_{\text{liq}}\Delta H)t \quad (7)$$

where κ_{vap} is the heat conductivity at vapor temperature at the interface T_{s} ; T_{b} is the temperature at the spherical walls of a container. This equation works even when there is a large temperature jump at the interface. Interestingly, eq. 6 reduces to eq. 7 only for the Lewis number (defined as the dimensionless ratio of thermal diffusivity to mass diffusivity) equal to unity [19], provided that we identify T_{vap} in eq. 6 with T_{b} in eq. 7. Equation 7 does not work in the case of evaporation into vacuum. Also, eq. 7 requires modifications, when the evaporating liquid has a direct contact with the hot stage.

From recent works emerged new rules which govern dynamics of irreversible pathway of evaporation. The evaporating mass flux is primarily governed by the energy balance (evaporation enthalpy must be balanced by a heat flux or heat capacity and temperature change) and mechanical equilibrium irrespective of a particular realization of the process (even when a droplet heated by a laser evaporates into the vacuum). The transport of heat is much slower than the transport of momentum. Therefore, density and temperature have to adjust to the condition of mechanical equilibrium. Most probably, even when the process is not quasi-stationary the irreversible pathway of evaporation follows a fast trail toward mechanical equilibrium. More work is needed to elucidate all aspects of this industrially important process and put it on a firm basis.

There are many issues that have not been raised in this short paragraph: the Leidenfrost effect, which probably will be of great importance in the nanoscale cooling systems; influence of convection on evaporation flux [14]; explosive boiling [14]; etc. Other examples of dynamic pathways in irreversible processes which still require a lot of study include two other common examples of condensation [17] and phase separation [20]. The condensation process is never quasi-stationary, it proceeds orders of magnitude faster than evaporation and leads to high temperatures inside condensing bubbles. Such condensing bubbles can be used as fast chemical microreactors at ambient conditions with temperatures inside a bubble reaching a few thousands K on a time-scale of 50 ps [17]. Also, only recently some mechanisms of very late stages of the phase separation process have been identified, such as: gravitational sedimentation and ‘‘collective Lifshitz–Slyozov’’ mechanism [20].

NONEXTENSIVE SYSTEMS

In classical thermodynamics, we divide the system into subsystems and introduce the notion of extensive and intensive thermodynamic variables which describe the equilibrium state of the system. Any extensive thermodynamic variable E has the following addition property:

$$E = \sum_i^N E_i \quad (8)$$

where N is the number of subsystems and E_i is the value of the thermodynamic variable for i -th subsystem. This tacit assumption of thermodynamics was completely ignored in the 19th century by Kelvin and other scientists who formulated a postulate of the final fate of the universe—its heat death associated with the state of maximum entropy. The universe as a whole, whose evolution is governed by long-range gravitational forces, cannot be described by classical thermodynamics, because such a system is nonextensive, i.e., it violates eq. 8. Similarly, a system of charges of one sign interacting via the long-range Coulomb potential is also nonextensive, i.e., it cannot be divided into proper subsystems as defined in classical thermodynamics. Thus, nonextensive systems can only be described by functions which do not have proper densities. Their entropy is a global property. The new approach to such systems is called nonextensive thermodynamics [21–24] based on the Tsallis or Renyi entropies [25,26]. We consider a system in a phase space described microscopically by point x in this space and define the probability density in the phase space as $p(x)$. The Tsallis entropy is defined as follows:

$$S_T^q(p) = \frac{1 - \int p^q(x) dx}{1 - q} \quad (9)$$

while the Renyi entropy has the following form:

$$S_T^q(p) = \frac{\ln \int p^q(x) dx}{1 - q} \quad (10)$$

The parameter q measures the degree of nonextensivity and in the limit of $q \rightarrow 1$, Tsallis and Renyi entropy reduces to the well-known form of the BGS entropy

$$S_{\text{BGS}}^q(p) = - \int p(x) \ln p(x) dx \quad (11)$$

BGS entropy is extensive, i.e., if we divide the system into two subsystems 1 and 2, we get

$$S = S_1 + S_2 \quad (12)$$

where S is the BGS entropy for the whole system and S_i is the entropy for the i -th subsystem $i = 1, 2$. This is not the property of Tsallis or Renyi entropies. Both are useful in the analysis of some stochastic processes and systems far from equilibrium [25,26], yet they do not constitute a part of the larger framework similar to classical thermodynamics and statistical mechanics.

SYSTEMS WITHOUT EQUILIBRIUM STATES

In the framework of classical thermodynamics, a number of assumptions are made. Before formulating these assumptions, we introduce the notion of isolated system, subsystems, equilibrium states, and thermodynamic limit, i.e., a limit of large system where boundaries do not appreciably influence the thermodynamic state of the system. These concepts constitute a basis for the main assumption in thermodynamics and consequently to the laws of thermodynamics. The main assumption of thermodynamics can be stated as follows: “every isolated system will sooner or later reach the state of thermo-

dynamic equilibrium, i.e., a state whose properties do not depend on time and which does not carry persistent fluxes". How can we relate this basic postulate to the living organisms? We could call a living organism a very complex nonequilibrium state, as did Prigogine. One observation, however, precludes it: we cannot move this system to the equilibrium state and back to the nonequilibrium living state, since along this pathway a living organism would encounter a highly irreversible process of death.

A living system cannot be isolated, because by definition it is open or actually semi-open. Thermodynamic limit does not apply to this system, because by definition it is finite and bounded by a surface. This surface strongly influences properties of the living system in the bulk, since all fluxes of matter and energy pass via the surface. Without them the system would be dead. The living system might have a stationary state, but certainly not an equilibrium state. Living organisms are also nonextensive and cannot be divided into parts, with same properties. Thus, instead of calling living matter systems far from equilibrium, I prefer to call them systems which do not have equilibrium states. It does not mean that we cannot analyze parts of the living system using methods of thermodynamics: all elementary reactions which occur inside the system have the proper equilibrium state, yet the organism as a whole does not have it.

The change of name from far-from-equilibrium to deprived-of-equilibrium is not only a semantic trick. It shows that in order to describe living matter in a holistic approach we need new language and paradigms different from those which we have used so far in thermodynamics. We can visualize a living organism as a set of strongly interconnected elementary modules. Each module, e.g., elementary first-order reaction, can be analyzed using the language of thermodynamics, equilibrium constant, etc. The connections between the modules, which form, e.g., a biochemical cycle, can also be characterized by detailed balance conditions. Yet at some higher level of interconnection, we need new language in terms of fluxes rather than thermodynamic forces, which would distinguish various states of the living organism and select some reference states for the system.

CONCLUSIONS

In the book *End of Science*, John Horgan [27] expresses a rather pessimistic point of view that humanity has reached a state where major scientific progress is no longer possible. Paradoxically, one of the reasons, he argues, for the end of science is the tremendous success of science in the past. Quantum mechanics, cosmology, and molecular biology paved a way to our understanding of the universe and life and pushed the frontiers of science to an unimaginable scale of space and time. All the examples presented in the book illuminate a stagnation point in the progress of science. Limited by space, time, and the finite speed of light, humanity does not seem to be able to use discoveries in femtosecond scale or properties of stars or planets light years from earth. Moreover, the basis of our understanding is set firmly and no new discoveries are possible—such a message flows from Horgan's book.

In my article, concerning only a small part of science, thermodynamics, I tried to present a different point of view—that we live in a world full of mysteries, which wait to be illuminated. The examples chosen in this text reflect my personal taste and interests, probably any scientists working in thermodynamics or statistical mechanics would give a different set of examples. The progress in thermodynamics is most certainly related to irreversible processes which for such a long time have waited to be properly described. One route in this direction was given a long time ago by Boltzmann and Maxwell in the form of the kinetic theory of gases; by Smoluchowski and Einstein, two founders of stochastic processes; Onsager and Prigogine, founders of irreversible thermodynamics. Another route has been recently paved by Jarzynski, and in another direction by Tsallis and Renyi. The dynamic pathway of evaporation in this context seems a trifle, yet it illustrates well one point: limitation of our knowledge based on speculations and the amount of speculations even in seemingly well-established science. I have no doubt that discoveries in the field of irreversible thermodynamics will bring us closer to the proper description of systems without equilibrium states and most certainly that knowledge will be used by humanity in a way unexpected by us today. And more importantly, only when humanity stops ask-

ing questions will we witness the end of science—and contrary to the message from Horgan's book, we keep asking questions and keep questioning established speculations.

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