

Steady State Thermodynamics

Yoshitsugu OONO and Marco PANICONI

Department of Physics, University of Illinois at Urbana-Champaign, IL, U. S. A.

(Received December 21, 1997)

A phenomenological framework corresponding to equilibrium thermodynamics is constructed for steady states. All the key concepts including entropy are operationally defined. If a system is strictly linear, the resultant Gibbs relation justifies the postulated form in the extended irreversible thermodynamics. The resultant Maxwell's relations and stability criteria give various le Chatelier-Braun type qualitative predictions. A phenomenological fluctuation theory around steady states is also formulated.

§1. Introduction

We will construct a phenomenological framework (steady state thermodynamics or SST) to organize macroscopic phenomena in steady states away from equilibrium. We wish to accomplish the goal as operationally as possible. Due to the nature of the problem, we must carefully analyze many 'dry' ingredients. Therefore, to make the paper easy to read, its structure is made more explicit than the usual papers with numerous subheadings.

Equilibrium statistical mechanics has its ultimate justification in its compatibility with equilibrium thermodynamics.¹⁾ After all, Gibbs²⁾ looked for a statistical system compatible with equilibrium thermodynamics. Phenomenology must give an important insight into the underlying statistical framework. Furthermore, without thermodynamics, practical relevance of statistical mechanics should have been much less than actually is: most partition functions cannot be computed especially for complicated systems relevant to, e.g., chemical plant designs.³⁾

Existing approaches

There have been attempts to extend thermodynamic framework to nonequilibrium states.⁴⁾⁻⁷⁾ Jou and coworkers are establishing the extended irreversible thermodynamics.⁸⁾ There are also systems proposed by Eu,⁹⁾ Keizer,¹⁰⁾ etc. These contributions attempt to write down the generalized Gibbs relation and to formulate a general phenomenological framework applicable to (time-dependent) systems away from equilibrium. Anyone interested in nonequilibrium statistical frameworks must pay due attention to Landauer's criticism.¹¹⁾

What is the difference between our approach and the existing ones?

We study, for simplicity, only time-independent steady states. It is questionable to have a reasonably small phenomenological state space for arbitrary time-dependent phenomena. Generalized or nonequilibrium entropy has never been operationally defined unambiguously. More generally speaking, we feel that operational approaches have been rare in non-equilibrium statistical physics. For example, in

order to introduce entropy operationally in equilibrium thermodynamics, the concept of adiabaticity is necessary. However, we have never seen any corresponding argument in nonequilibrium phenomenologies. We wish to introduce all the concepts and quantities operationally in our approach.

Is ‘thermodynamic formalism’ relevant?

The thermodynamic formalism for dynamical systems¹³⁾ has been used to establish a phenomenological framework,^{14), 15)} but it is essentially a fluctuation theory around a given state, because large deviation theory¹⁶⁾ does not generally compare two different dynamical systems (e.g., dynamical systems with different control parameters). In contrast, the main aim of equilibrium thermodynamics is not to study fluctuations but to compare two different states under different values of control parameters, e.g., temperature, pressure, etc. Hence, the name ‘thermodynamic formalism’ in the theory of dynamical systems is misleading.

Outline of the paper

In § 2, we quickly survey the reasons why we believe there is a phenomenological framework for steady states. In § 3, we discuss the general form of the theoretical framework, and claim that we have only to look for a natural extension of equilibrium thermodynamics. In § 4, we set up the state space for our phenomenological description of steady states. The most crucial concept in equilibrium thermodynamics is adiabaticity. We need a corresponding concept for open systems. Section 5 prepares for the introduction of s-adiabaticity (steady adiabaticity). After these preparations, in § 6, main postulates of steady state phenomenology are given which correspond to the principles of equilibrium thermodynamics. In § 7, operational feasibility is summarized. Section 8 discusses some consequences of the stability criterion such as the nonequilibrium version of Le Chatelier-Braun’s principle. Section 9 is the phenomenological fluctuation theory around steady states. Section 10 is for concluding remarks.

§2. Possibility of phenomenology

There are several reasons to believe that there is a “thermodynamic” (or macroscopic phenomenological) framework for steady states.

General empirical facts

We know there are systems that eventually settle down to time-independent nonequilibrium states under constant conditions. In this paper, we focus our attention to such time-independent cases. It is empirically likely that the final state will never return spontaneously to the initial state. This is reminiscent of the second law in equilibrium thermodynamics.⁶⁾

Large deviation theoretical consideration

According to large deviation theoretical considerations,^{16), 14), 17)} the most probable steady state is characterized by a variational principle. It is natural to interpret

this variational principle as the stability criterion for the state derived from the analogue of the second law as in the ordinary thermodynamics.

How plausible is the existence of nonequilibrium entropy?

In a certain sense, the true equilibrium limit is a singular limit. For example, even if a slightest steady driving is applied to an isolated system, the system will be eventually red hot. However, if we can carefully remove the steadily produced heat due to dissipation (that we will call the house-keeping dissipation), then the state should not be very different from equilibrium (or at least there are many quantities that change continuously; recall that this is the fundamental assumption of linear response theory which seems to have been successful). Hence, it is not so outrageous to expect the extension of entropy level sets into nonequilibrium steady state space.

Microscopic considerations: Invariant measure in phase space

Even in a steady state of a system driven by an external field, there must be an invariant measure on the phase space.*) The measure should be absolutely continuous with respect to the phase volume. It is unlikely that we need extremely many parameters to characterize the measure, if the system is not very far away from equilibrium. Hence, there must be a coarse-grained characterization of steady states. This reasoning is logically out of place for a pure phenomenology point of view adopted in this paper, but if one expects a sort of statistical thermodynamic framework for steady states, it is a good reason to expect a phenomenological framework.

Nature of dissipation

Intuitively, the transfer of energy from a systematic degree of freedom (say, a macroscopic flow) to microscopic degrees of freedom should be irreversible even under nonequilibrium conditions. Hence, the essence of dissipation should be the same in equilibrium and in nonequilibrium. Of course, under appropriate nonequilibrium conditions, we may be able to organize a small fraction of microscopic motions into a macroscopic motion as dissipative structure illustrates. However, this must be at the expense of increasing microscopic disorder somewhere else. Thus it is likely that there is a nonequilibrium version of Kelvin's principle.

Aim of phenomenology

Although to obtain some information about the statistical ensemble describing nonequilibrium steady states is an important goal, the main aim of this study is to make a framework which can relate macroscopically observable facts and data. To pursue the consequences of stability/evolution criteria is also an important aim. The relation between the input and output power/heat rate is not directly studied in our framework, because we study only the state variables of the system. However, through the properties of the system the input to and output from the system would

*) However, we must note that if there is a material flux going through the system, we do not have purely dynamical descriptions, so that this argument does not apply.

be related indirectly.

Distributed systems

Since nonequilibrium systems are very often spatially nonuniform distributed systems, the ultimate usage of our phenomenology is in the differential (spatially local) form just as in the case of the conventional nonequilibrium thermodynamics.¹⁸⁾ Therefore, we will have to assume the local steady hypothesis. However, this should be more realistic than the local equilibrium hypothesis.

§3. Possible form of phenomenology

We begin with a review (reorganization) of equilibrium thermodynamics, and then claim that all the physics theories can be cast in the thermodynamic form.

Standing assumption: the fourth law

Throughout this paper we assume the fourth law:⁷⁾ there are only extensive and intensive quantities in thermodynamics, to be applicable to our phenomenology as well. We should keep it in mind that without the fourth law it is difficult to justify the relevance of ensemble theory to real physics.¹⁶⁾ Notice that there is no reason to deny *a priori* the fourth law even for non-Gibbsian ensembles. Fluctuations in such systems are expected to be highly nonlocal,¹⁹⁾ and there seems to be a good analogy with dipolar equilibrium systems.²⁰⁾ That is, the fluctuation statistics depends on the domain shape on which we observe fluctuations of state variables. We expect, however, that in contrast to the equilibrium dipole systems, the averaged quantities (state variables) are not domain-shape dependent.

A summary of equilibrium thermodynamics

As an example of a very successful phenomenology, it is useful to summarize the principles of equilibrium thermodynamics with de-emphasizing temperature:

ThO If isolated, a system eventually reaches a (macroscopic) state which can be specified uniquely by variables (called state variables) $\{E, X_i\}$, which span the state space.

ThI There is a 1-form (called the heat form) $\omega = dE - \sum f_i dX_i$, where f_i are functions of state variables, and $\omega = 0$ is realizable (this process is called a quasiequilibrium adiabatic process).

ThII In any small neighborhood^{*)} there is a state which cannot be reached by a quasiequilibrium adiabatic process.

The third law could be added as a statement about the integrating factor for the heat form. In this formalism, state and state variables $\{E, X_i\}$ are primitive concepts as points and lines in Euclidean geometry. Equilibrium thermodynamics asserts that for a given system there are states for which we can choose 'state variables' such that **ThO-II** hold.

^{*)} We do not specify the topology of the state space formally.

Entropy

From **ThII** we assert that ω has an integrating factor locally in the state space:^{21), 22)} There is an objection by Bernstein²³⁾ that Caratheodory's argument²⁴⁾ is not enough to establish the global existence of a smooth integrating factor (and smooth entropy level sets). He used the equivalence relation of thermal equilibrium stated in the standard version of the zeroth law to overcome the difficulty. If we do not assume this equivalence relation, we can proceed further as follows with the aid of the fourth law. Note that if $\omega = \lambda d\sigma$, then another integrating factor λ^* may be related to the original one as $\lambda^* = \lambda/(d\varphi/d\sigma)$, where φ is a smooth function.*) Now, we rely on the fourth law: λ must be an intensive function and σ must be extensive. This should remove the ambiguity of the integrating factor except for the choice of the units. To proceed further, in equilibrium, we need a thermometer, so that actually we must use the conventional zeroth law. In the case of steady states, its consistency with equilibrium thermodynamics removes the remaining ambiguity.

Maximum principle for entropy

Under adiabatic conditions, the maximum principle for entropy characterizes the state in the usual equilibrium thermodynamics. In order to assert this **ThII** above is not enough. We need a statement about non-quasiequilibrium processes (irreversible processes) such as Clausius' principle.

Thermodynamic formalism

The reader may criticize that restating thermodynamic principles in an abstract fashion will not take us anywhere. As is illustrated below, however, any theory of physics with a variational principle can be cast in this 'thermodynamic framework'. In particular, we have only to pay attention to a certain 1-form. A key observation is: a forbidding principle implies a variational principle as explicitly recognized by Caratheodory.²⁴⁾ We wish to call this framework (phenomenological) thermodynamic formalism.

Thermodynamic formalism for classical mechanics

Take classical mechanics of a single particle as an example. Its state is specified by its position q at a given time t . Hence, (t, q) spans the state space (traditionally called the world). The (phenomenological) thermodynamic formalism for classical mechanics reads as follows:²⁶⁾

CI There is a 1-form $\omega = dt - (p/H)dq$, where p is the conjugate momentum, and H the Hamiltonian, and $\omega = 0$ is realizable.

CII In any small neighborhood of a state in the state space, there is a state which cannot be reached by a vanishing Lagrangian process.

The adiabatic process requires $Hdt = pdq$ or $H = 2T$, where T is the kinetic energy. That is, $T - V = 0$, where V is the potential energy. For any neighborhood of (t, q) , obviously there is a state which cannot be reached by a trajectory with

*) We only pay attention to smooth factors, and, as in the elementary thermodynamics, we assume all the quantities are differentiable for simplicity, ignoring difficulties due to phase transitions.

Lagrangian = 0. Hence, as everyone knows, ω has an integrating factor: $\omega = dS/H$, where S is the action.*) The Maxwell relations give Hamilton's canonical equations of motion. $H = \infty$ corresponds to the absolute zero, and Hamilton's principle corresponds to the Gibbs principle in equilibrium thermodynamics.

Since classical mechanics can be cast in the (phenomenological) thermodynamic formalism, obviously all fundamental theories of physics, e.g., quantum mechanics, electrodynamics, can be cast in this form.

Comparison of classical mechanics and thermodynamics

The zeroth law is not stated in the above formulation of classical mechanics, because we cannot get out of the world classically. In classical mechanics we do not consider a path outside the world (off-shell path) corresponding to the nonequilibrium path in equilibrium thermodynamics. This is a distinction of classical mechanics from equilibrium thermodynamics, where irreversible processes are extra-state-space processes (off-shell processes). Because of this the variational principle for classical mechanics is an extremum principle, while that for thermodynamics is a maximum principle. This is also related to the fact that t is not bounded, but E is bounded from below. It is an intriguing possibility that the off-shell path in classical mechanics could be connected to quantum mechanics (recall that thermodynamic fluctuation theory is an off-shell theory). Also the Lorentz invariance of action S may suggest some sort of transformation invariance of thermodynamic entropy in the state space.

What sort of phenomenology should we seek?

Our aim is to find a phenomenological framework to describe steady states. We wish to have a stability or evolution criterion as in the equilibrium counterpart, so the phenomenology we seek should have a variational principle. The above consideration tells us that in order to obtain a desirable phenomenology we have only to look for a framework in quite a parallel form to the ordinary thermodynamics. We are not *a priori* asserting that there is such a phenomenology. However, we can assert that if we fail to find a consistent phenomenology in this way, we may conclude that there is no interesting phenomenology for steady states. Whether our phenomenology proposed below is consistent or not will ultimately be decided empirically.

§4. State space

As is stated above, the concept of state space and state variables are primitive concepts, so that whether they are well-defined or not must ultimately be checked by experiments. The choice of state variables is not a trivial question even in equilibrium thermodynamics. If we overlook a thermodynamic coordinate (i.e., a thermodynamic degree of freedom), then thermodynamics does not hold (e.g., **ThII** does not hold).

e- and n-variables

For simplicity, in this paper, we discuss mostly spatially uniform systems

*) The choice of the integrating factor is not unique. To choose the one we adopted here, we need an additional requirement, e.g., the integrating factor is additive.

(systems through which various flux are uniform even in steady states). Let us write its equilibrium state variables (henceforth we call them e-variables) as usual E and X_i , where E is the total energy of the system, and X_i are the usual equilibrium extensive quantities such as volume, magnetization, etc. These extensive variables are the total amount of microscopically well-defined quantities, so that even in a nonequilibrium steady state they are meaningful, and operationally well defined (experimentally observable).

If the system is not in equilibrium, it is obvious that e-variables are not enough to describe the state even macroscopically. At least we need a variable which distinguishes a nonequilibrium state from the equilibrium state sharing the same e-variables. We call the extra nonequilibrium extensive variables Y_i needed to specify the state n-variables. Henceforth, e- and n-extensive variables X_i and Y_i are collectively denoted by Z_i .

Simple steady state

We call a steady state a simple nonequilibrium steady state, if it requires only a few (ideally only one) n-variables Y_i to specify it macroscopically.

For example, consider a thin fluid layer sandwiched between plates moving with different constant velocities. The fluid layer is sheared with a constant shear rate. Until the laminar flow becomes unstable, it is likely that we need only one n-variable. This could be the (negative)^{*} generating rate Q_H of heat due to dissipation or nonequilibrium displacement. This $(-)Q_H$ is the dissipation needed to maintain the state (the house-keeping cost).

Multiple steady states, etc.

It is well known that nonequilibrium systems can have many multiple steady states under a given condition. However, this is not a problem peculiar to nonequilibrium states. We also have metastable states in equilibrium. We must admit that under nonequilibrium conditions the influence of microscopic noise may be reduced, so that we may suffer much more from having metastability than in equilibrium. Still, it is not a fundamentally new problem to steady states. Besides, we do not pay attention to systems locally very far away from equilibrium in this paper.

Also we should not forget that nonequilibrium steady states are, generally speaking, not isotropic due to flux, even though the system is isotropic in equilibrium.

§5. Slow processes and quasisteady processes

Slow process

Slowing down the changing rate of state variables indefinitely, we can make all the instantaneous states during a process as indistinguishable as possible from steady states in the state space (of steady states).

Let us call a process which can be regarded lying in the state space (so that at each instant the state is indefinitely close to some steady state) a slow process.

^{*} Sign convention: + implies that heat is flowing *into* the system and – the opposite.

The slowness required in the slow process is the slowness of the modification (or the change due to perturbation) of possibly rapid processes. Therefore, dissipation due to the process produces heat that may have to be discarded sufficiently promptly to its environment in order to maintain its steady state.

Distinction between equilibrium and nonequilibrium processes

In equilibrium thermodynamics, a process whose path is in the state space is called a quasiequilibrium process. Operationally, the process is realized by sufficiently slowing down the changing rate of state variables. Suppose we change a system more or less uniformly in time during the time span of Δt . Because the dissipation rate (production rate of entropy) is proportional to the square of the rate of change $(\Delta t)^{-1}$, the total entropy production is proportional to $(\Delta t)^{-2} \times \Delta t = (\Delta t)^{-1}$. That is, slowing down can indefinitely decrease the total entropy production. This is the reason why slow processes become quasiequilibrium, so that any process which is in the state space can be used to compute the entropy change.

However, if a system is in a nonequilibrium steady state driven by an external driving force, the change in energy dissipation rate (consequently, the change in entropy production rate, if entropy is meaningful) is proportional to $(\Delta t)^{-1}$, because it is proportional to the changing rate times the driving force which is away from zero already. (Note that here we consider only the changing portion of dissipation, ignoring the already existing house-keeping dissipation for the initial steady state.) This implies that slowing down cannot indefinitely decrease the total energy dissipation caused by the change. This is a marked distinction between driven steady states and equilibrium states.

Quasisteady process

As is well known, the total heat absorption depends on the path in the state space even if we fix both ends of the path. In nonequilibrium the preceding consideration tells us that the absorbed heat during the process is not even determined by the path in the state space in contrast to equilibrium cases; the heat depends further on how we proceed along a given path (on how we realize a given slow process path, or on the realization protocol for a given path). Therefore, if we interpret the quasiequilibrium process in the equilibrium state space as the least dissipative process, then a slow process in the steady state space is not always a reasonable nonequilibrium analogue of the quasiequilibrium process.

Let us call a slow process along a given path in the state space with the smallest dissipation a quasisteady process along the path. Thus for each path in the state space we have a quasisteady process. Experimentally, we can monitor the generated heat during the specified slow process path in the state space. Therefore, in principle, we can realize such a process. However, we must properly take care of the house-keeping heat as follows.

Need of 'renormalizing' total heat production

Although an 'official' definition of a quasisteady process is in terms of minimum

heat generation, since we are in a nonequilibrium state, even to fix the system at a given point in the state space (i.e., to maintain a steady state), we dissipate energy as heat (the house-keeping heat). Hence, if a process is done infinitely slowly, then the total generated heat during the process becomes infinitely large. We must somehow subtract the contribution of the house-keeping heat, if we wish to realize the minimization process. We wish to introduce the concept of excess heat after ‘renormalizing the infinity’.

Excess heat

We can certainly measure the input power P due to driving and the actual heat importing rate Q_A (sign convention: + implies that heat is flowing into the system and – the opposite) of the system at each instant along a path corresponding to a slow process which lies in the state space. The house keeping heat rate Q_H is (–) the heat generation rate of the instant state lying along this path. The (–) excess heat generation rate is defined as

$$Q_{\text{ex}} \equiv Q_A - Q_H. \quad (5.1)$$

This gives the needed ‘renormalization’ of the generated heat. For a process of duration t ,

$$\Delta E = \int_0^t (P + Q_A) dt \quad (5.2)$$

is the total net energy absorbed by the system during the whole process. This is obviously measurable. Q_H is of course measurable, so that we may construct

$$\Delta E' = \int_0^t (P + Q_H) dt. \quad (5.3)$$

ΔE and $\Delta E'$ are both finite even in the $t \rightarrow \infty$ limit. Now, we can make the difference of these two to obtain

$$q_{\text{ex}} = \Delta E - \Delta E' = \int_0^t (Q_A - Q_H) dt = \int_0^t Q_{\text{ex}} dt. \quad (5.4)$$

We take the slow limit $t \rightarrow \infty$ to obtain the excess heat q_{ex} for the given path (and its protocol). To be quasisteady, we must search for the minimum of this quantity for the given path over various protocols. This is in principle feasible, but a practical method may be proposed as follows.

Practical realization of quasisteady process

Suppose the state B can be reached from A by increasing the driving which causes an increase of systematic power supply. In this case, it is very likely that the slow limit of systematic power supply increase gives a quasisteady process from A to B (while controlling the state variables by modifying the e-variables gently and also controlling the heat discarding rate).

When deceleration is required, the situation is much more complicated. Although, in principle, a quasisteady process should be reversible (can be retraced), to realize it in practice is generally hard. Consider a flow which becomes chaotic upon

driving. Even if the flow is chaotic the motion is macroscopic, so that the flow kinetic energy can be completely taken out from the fluid system as work, in principle. Of course, this is impossible in practice. However, it is still true that the chaotic motion is not a microscopic motion so that ‘thermodynamic entropy’ of the system should not be affected by the motion (unless it affects the microscopic order).

It is an intriguing possibility of taking this impossibility at its face value to construct a phenomenology at the mesoscopic level, perhaps phenomenology of turbulence. However, here, we concentrate on the situation where macro-micro distinction is more or less clear. Hence, even if the retracing of quasisteady process is impossible in practice, we do not pay serious attention to it.

Meaning of excess heat

The house-keeping heat rate Q_H does not account for the total energy difference ΔE between different steady states. Hence, q_{ex} measures the net energy imported to the hidden degrees of freedom in Callen’s terminology.²⁵⁾ $\Delta E - q_{\text{ex}}$ is the remaining systematic part called (excess) work that is described by the change of Z_i variables, that is, the portion of energy stored in the system in the systematic form.

Adiabatic quasisteady process

Let us call a process described by a path in the state space (i.e., slow process) with $Q_{\text{ex}} = 0$ (recall that upper case Q always denotes import *rate*) along the path s-adiabatic process (or simply adiabatic process if there is no ambiguity). If ‘the minimum $Q_{\text{ex}}' = 0$, the process is called an adiabatic quasisteady process.

§6. Postulates for steady state phenomenology

Existence of quasiadiabatic steady process

That there is an adiabatic quasisteady process is, strictly speaking, still a postulate. However, since we can imagine processes with positive and negative excess heats, it is plausible by continuity that there must be an s-adiabatic process.

Postulates for phenomenology

It is highly plausible that in any neighborhood of a steady state in the state space there is a steady state which cannot be reached by a quasisteady s-adiabatic process.

SO If left unperturbed (in a fixed environment), a system reaches a (macroscopic) state which can be uniquely specified by extensive variables (=observables) $\{E, Z_i\}$, which span the state space.

SI There is a 1-form (called the excess heat form) $\omega = dE - \sum h_i dZ_i$ for which a process $\omega = 0$ is realizable. Here h_i are functions of E and Z_i . (This process is called a quasisteady s-adiabatic process.)

SII In any neighborhood of a state in the state space, there is a state which cannot be reached by a quasisteady s-adiabatic process.

As usual, and as stated before, we assume E and Z_i are extensive quantities. E is the total energy of the system in this exposition. Our general discussion on

phenomenological thermodynamic formalism in § 3 cannot immediately tell us what state variables we should choose. Therefore, the above choice of E is an extra hypothesis. Other choices might be more adequate if the system is very far away from equilibrium. However, for conventional materials scientific problems our choice seems admissible according to the conclusions we can draw from this choice as seen below.

We know **SO** is not always true. Our framework is designed only for systems reaching time-independent steady states eventually.

We write

$$dE = \theta d\Sigma + f_i dX_i + g_i dY_i, \quad (6.1)$$

where Σ is entropy. We should use S instead, because it is a natural extension of the ordinary entropy and is identical to the latter in the equilibrium limit, but here in order to stress the difference of equilibrium and nonequilibrium, we use different symbols. The postulate **SII** alone cannot uniquely specify θ . However, as discussed already, if we assume the continuity of θ , then the only ambiguity is the choice of the unit (i.e., numerical factor). This is fixed by the requirement that in the equilibrium limit Σ must be identical to the equilibrium entropy. Therefore, precisely speaking, we should explicitly declare that we assume all the postulates of equilibrium thermodynamics for equilibrium systems.

Stronger form of second law

The generalized version of the second law here **SII** is in a weak form, which asserts the foliation of the state space into isentropic hypersurfaces. We wish to have a maximum principle or the principles specifying the natural direction of change as the usual second law. We must mention non-quasisteady processes. At least we can do this for slow processes with the aid of a generalized Thomson's principle: **SIIT** A process converting work into excess heat is irreversible.

Here 'work' means a systematic way to transfer energy (not to hidden degrees of freedom in Callen's words²⁵⁾) to the system. 'Reversibility' is modulo house-keeping heat, which is produced anyway.

§7. Operational feasibility

Adiabatic continuation of entropy level set

Starting from an equilibrium state whose entropy is known, we can go to a nearby steady state which can be reached by a quasisteady process which is s-adiabatic. In this way, we can extend constant entropy level sets into steady state space.

Gibbs relation

We have already discussed Σ in the preceding entry. Since we can construct the level sets, we can measure Σ . E is the total energy of the system, so it should be measurable in principle with the aid of equilibrium thermodynamics. We can measure all the Z_i variables. Hence, the derivatives of E with respect to Z_i and Σ are accessible operationally. Consequently, we may conclude that all the quantities

in the generalized Gibbs relation (6.1) are operationally well-defined (i.e., experimentally measurable).

General formula for strictly linear systems without memory

Let Y be a flux (vector) (n-variables) which obeys the following linear dynamics

$$L \frac{dY}{dt} = -RY + h, \quad (7.1)$$

where L and R are matrices, and h denotes conjugate variables. The power introduced to the system is given by $P = h'Y$ (' implies transposition), and the house keeping heat rate is given by $Q_H = -Y'RY$. Assume that there is no hidden coordinates which absorb energy. Then, the actual heat discarding rate and $|Q_H|$ must be the same. Hence, the total energy increase of the system ΔE can be written as

$$\Delta E = \int dt(P + Q_H) = \int dt Y'(h - RY) = \Delta \left(\frac{1}{2} Y'LY \right) = \Delta \left(\frac{1}{2} Y'R\tau Y \right), \quad (7.2)$$

where τ is the relaxation time matrix $\tau \equiv R^{-1}L$. Here, the meaning of the R matrix is clear from the steady relation $h = RY$. It is the inverse response matrix. The contribution of these n-variables Y to the Gibbs relation reads

$$dE = \dots + Y'R\tau dY, \quad (7.3)$$

where \dots denotes the usual equilibrium terms. This is the generalization of the formula postulated by Jou et al.⁸⁾ for their extended irreversible thermodynamics. Needless to say such a simple formula works only when all the responses are strictly state-independent.*)

Critique of previous approaches to nonequilibrium entropy

Nonequilibrium generalizations of entropy or related concepts have been considered by many people. A notable example due to Jou et al.⁸⁾ reads

$$S_{\text{neq}} = S_{\text{eq}} - \int \sigma dt, \quad (7.4)$$

where σ is the entropy production rate during the quenching process of the irreversible processes in an adiabatic bomb. S_{eq} is the entropy of the final equilibrium state. The formula is intuitively appealing, and indeed contains a grain of truth, but the actual formula for Σ of a state even close to equilibrium is not this simple. The main difficulty is that relaxation process is not quasisteady, so that it cannot generally be used to compute the entropy change.**) Thus, it is quite unlikely that a simple bomb experiment can actually give the difference between Σ and the entropy

*) We can extend this simple result to the case with memory effects. In this case $Y'R\tau\delta Y$ is replaced by $\int dt Y'R * \delta Y$, where $*$ is the time convolution.

**) If strictly linear, the formula is correct. That is, if there is no effect of the change of Z variables on the transport coefficients. This is unlikely, because the system 'temperature' increases upon quenching.

of the nearby equilibrium state. Consequently, (7.4) cannot generally be true. However, Jou et al. instinctively know this problem, and they never apply this blindly when they compute nonequilibrium entropy deviation from its nearby equilibrium state values. According to their general result, $S_{\text{eq}} - \Sigma \propto \tau J^2$, where S_{eq} is the fictitious entropy when all the nonequilibrium effects are turned off without any effect on static variables, and τ is the microscopic relaxation time of the flux J (not the relaxation time of the macroscopic flow).

§8. Evolution and stability criteria

Evolution and stability criteria

According to the generalized Thomson principle **SIIT**, we realize that a spontaneous change under s-adiabatic condition is

$$\delta\Sigma > 0. \quad (8-1)$$

More generally, the evolution criterion is

$$\delta\Sigma > \delta q_{\text{ex}}/\theta, \quad (8-2)$$

so that the stability criterion is

$$\delta\Sigma \leq \delta q_{\text{ex}}/\theta = \theta^{-1}[\delta E - f_i \delta X_i - g_i \delta Y_i]. \quad (8-3)$$

Here intensive variables are assumed to be kept constant (externally given).

Notice that the variational principles related to entropy production⁴⁾ are not the variational principles for the distribution function of the state, but about the large deviation from it. Hence, for example, the principle of minimum entropy production is not directly related to the Gibbs relation. That is, it cannot determine the steady measure.

Consequence of convexity

The convexity of energy as a function of extensive variables (Σ and Z_i) implies that the following matrix is a nonnegative definite matrix:

$$\text{Matr.} \left[\left(\frac{\partial h_i}{\partial Z_j} \right) \dots \right], \quad (8-4)$$

where \dots denote Z_k other than Z_j .

Entropic and energetic steady states

We can classify nonequilibrium steady states of simple systems into entropic nonequilibrium states and energetic nonequilibrium states according to the sign of $(\partial\Sigma/\partial Y)_\theta$, where Y is the power dissipation. We say a steady state is entropic, if

$$\left(\frac{\partial\Sigma}{\partial Y} \right)_\theta < 0 \quad (8-5)$$

and energetic, if the inequality is reversed. If a state is entropic, the entropy decreases when the system is driven away from equilibrium under constant θ (\sim temperature if not far away from equilibrium).

For example, we obtain for an entropic state

$$\left(\frac{\partial g}{\partial \Sigma}\right)_Y \left(= \left(\frac{\partial \theta}{\partial Y}\right)_\Sigma\right) > 0. \quad (8.6)$$

Hence, for entropic nonequilibrium states the time scale of microscopic relaxation increases as the microscopic order of the system decreases, if the dissipation is maintained.

Le Chatelier-Braun principle

From the stability condition (the convexity of the total energy) with the aid of the standard argument used in equilibrium thermodynamics, we conclude the following Le Chatelier-Braun principle:²⁷⁾

$$|(\Delta Z)_{Z'}| \leq |(\Delta Z)_{h'}| \quad (8.7)$$

and

$$|(\Delta h)_{Z'}| \geq |(\Delta h)_{h'}|, \quad (8.8)$$

where ' implies the conjugate pair other than (h, Z) . For example, we obtain

$$(\Delta Y)_\Sigma \leq (\Delta Y)_\theta. \quad (8.9)$$

§9. Phenomenological theory of steady fluctuation

Fluctuations around steady states have been studied in terms of Langevin equations and master equations. In equilibrium, these models are set up to satisfy the equilibrium condition. For example, the noise is chosen to satisfy the fluctuation-dissipation theorem. This is legitimate because we know the equilibrium phenomenology and statistics. Under nonequilibrium conditions, especially when the local equilibrium condition is violated, we do not have any reliable basis to check the validity of stochastic models. Hence, to use stochastic models to construct a phenomenological framework of nonequilibrium states, or, more generally, to study fundamental aspects of nonequilibrium statistical mechanics, is a questionable endeavor.

General hypothesis

Here, we mimic the thermodynamic theory of equilibrium fluctuations. It assumes an extra postulate, which reads, following Callen²⁵⁾ as:

The probability density p of finding extensive parameters X_i and Y_i to be at its instantaneous values \hat{X}_i and \hat{Y}_i is given by the generalized Boltzmann-Einstein relation:

$$p \propto \exp \frac{1}{k_B} (\Sigma - (f_i/\theta)\hat{X}_i - (g_i/\theta)\hat{Y}_i). \quad (9.1)$$

This is a postulate. This is for fluctuations around ensemble-averaged quantities, and is distinct from that for fluctuations²⁸⁾ around time-averaged quantities that may be more convenient for explicitly time-dependent states.

General expression for linear systems

For strictly constant coefficient linear systems, we know the general expression of the Gibbs relation

$$dE = \theta d\Sigma + \text{the usual equilibrium terms} + Y'R\tau dY. \quad (9.2)$$

Hence, the fluctuation probability reads

$$p \propto \exp\left(-\frac{\delta Y'R\tau\delta Y + \text{the usual equilibrium terms}}{2\theta}\right). \quad (9.3)$$

As in equilibrium no first order terms show up due to the stability of the steady state. Therefore, if we may ignore the correlation between the n and e fluctuations (the simplest case),

$$\langle YY' \rangle = L^{-1} = \theta(\tau^{-1}R^{-1})_+, \quad (9.4)$$

where + implies the symmetric part.*) If we may assume the ordinary temperature is meaningful, we may set $\theta = T$ (in energy unit).

§10. Concluding remarks

We have proposed an operationally feasible phenomenological framework, steady state thermodynamics (SST), for nonequilibrium steady states tantamount to equilibrium thermodynamics. SST is based on the principles just like those for equilibrium thermodynamics (justification has also been given of having this form if a phenomenological framework exists at all), and reduces to the latter in the equilibrium limit. In particular, operationally, we can measure (nonequilibrium) entropy away from equilibrium. The resultant formalism can give the Gibbs relation postulated by Jou et al. for strictly linear systems, although we have to point out that their proposal for measuring nonequilibrium entropy is not operationally complete. A phenomenological fluctuation theory is formulated as well. The current framework can predict qualitative behaviors, for example, whether the relaxation time of a system increases or not when its microscopic disorder increases under constant dissipation.

Acknowledgements

Critical comments of K. Sekimoto, S. Sasa and G. Eyink are gratefully acknowledged. The work is, in part, supported by the National Science Foundation grant DMR 93-14938.

*) If there is a memory effect, this becomes a Green-Kubo relation.

References

- 1) Y. Oono, *Statistical Thermodynamics in Encyclopedic Dictionary of Polymer Science* (Wiley, 1989), vol. 15, p. 614.
- 2) J. W. Gibbs, *Elementary Principles in Statistical Mechanics Developed with Especial Reference to the Rational Foundation of Thermodynamics* (Yale University Press, 1902).
- 3) G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substance* (McGraw-Hill, 1923).
- 4) S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, 1984).
- 5) D. D. Fitts, *Nonequilibrium Thermodynamics, a Phenomenological Theory of Irreversible Processes in Fluid Systems* (McGraw-Hill, 1962).
- 6) P. Glansdorff and I. Prigogine, *Thermodynamics of Structure, Stability, and Fluctuations* (Wiley-Interscience, New York, 1971).
- 7) P. T. Landsberg, *Nature* **238** (1972), 229.
- 8) D. Jou, J. Casas-Vázquez and G. Lebon, *Rep. Prog. Phys.* **51** (1988), 1105; *Extended Irreversible Thermodynamics* (Springer, 1993).
- 9) B. C. Eu, *Ann. of Phys.* **140** (1982), 341; *Physica* **A160** (1989), 53.
- 10) J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes* (Springer, 1987).
- 11) R. Landauer as summarized in *Physica* **A194** (1993), 551.
- 12) R. Landauer, *J. Stat. Phys.* **9** (1973), 351.
- 13) Ya. Sinai, *Russ. Math. Surveys* **29**(4) (1972), 21.
D. Ruelle, *Thermodynamic Formalism* (Addison-Wesley, 1978).
- 14) Y. Takahashi and Y. Oono, *Prog. Theor. Phys.* **71** (1984), 851.
See also Y. Oono and Y. Takahashi, *Prog. Theor. Phys.* **63** (1980), 1804.
- 15) G. Gallavotti and E. G. D. Cohen, *J. Stat. Phys.* **80** (1995), 931.
G. Gallavotti, *Phys. Rev. Lett.* **77** (1996), 4334.
- 16) J.-D. Deuschel and D. W. Stroock, *Large Deviations* (Academic Press, 1989).
Y. Oono, *Prog. Theor. Phys. Suppl. No. 99* (1989), 165.
- 17) G. Eyink, *J. Stat. Phys.* **61** (1990), 533.
- 18) K. Kitahara, K. Miyazaki and D. Bedeaux, *Physica* **A230** (1996), 600.
- 19) P. L Garrido, J. L. Lebowitz, C. Maes and H. Spohn, *Phys. Rev.* **A42** (1990), 1954.
- 20) F. J. Alexander and G. Eyink, unpublished.
- 21) M. Born, *Physik. Z.* **22** (1922), 218, 249, 282.
- 22) P. T. Landsberg, *Thermodynamics with Quantum Statistical Illustrations* (Interscience, New York, 1961).
- 23) B. Bernstein, *J. Math. Phys.* **1** (1960), 222.
- 24) C. Caratheodory, *Math. Ann.* **67** (1909), 355.
- 25) H. B. Callen, *Thermodynamics* (Interscience, 1960).
- 26) Y. Oono, mimeographed note (1974).
- 27) For example, L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon).
- 28) M. Paniconi and Y. Oono, *Phys. Rev.* **E35** (1997), 176.