

On the transition of a non-equilibrium system to an equilibrium system

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Received October 20, 2014 / Received in final form 7 May 2015

Published online 17 July 2015

Abstract. It is shown that the most important feature of Non-Equilibrium Thermodynamics is not the entropy production, but the organization of the currents in order to flow. This is also needed to obtain the maximum entropy in the equilibrium state, as is required by Equilibrium Thermodynamics.

This article is supplemented with comments by Hong Qian and Yves Pomeau and a final reply by the author.

It is a real privilege for me to contribute to this Festschrift in honor of Jacques Yvon.

In 1969, more than 45 years ago, he wrote a book about entropy: “Correlations and Entropy in Statistical Mechanics”¹. He was clearly an original, who thought for himself. In his book he uses a cluster-like expansion of the entropy, in order to obtain in a systematic way its space correlations.

In this paper I also want to write about entropy, as Yvon did, but I will discuss a different aspect of the equilibrium entropy, which leads to a new insight into this quantity.

The entropy was introduced into physics by Rudolf Clausius. It took him from 1854–1865 to straighten out this new concept to his satisfaction [1].

I want to discuss here the following question.

In a non-equilibrium system, according to Non-Equilibrium Thermodynamics, there are flowing currents, which must have dissipation or entropy production, according to the Second Law of Thermodynamics’ impossibility of a *perpetuum mobile* of the second kind. Otherwise one would have a machine, which would function eternally by absorbing heat from an (infinite) heat reservoir and using this heat completely to run this machine.

In order to create a non-equilibrium system from an equilibrium system, appropriate external forces have to be applied to the equilibrium system. Thus, e.g. to obtain from a system A in thermal equilibrium at a temperature T_A , a non-equilibrium system with a heat flux, one attaches to it two heat reservoirs of different temperatures $T_B > T_C$ (cf. Fig. 1). This temperature difference will create a temperature gradient in the original system A, leading to a heat current \mathbf{J}_A , from the high temperature

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¹ In this book also the so-called BBGKY (Bogolubov-Born-Green-Kirkwood-Yvon) hierarchy – a name coined by G.E. Uhlenbeck – can be found.

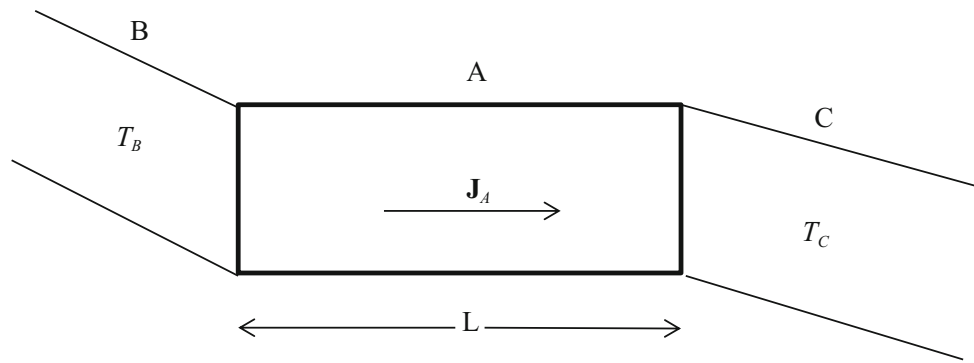


Fig. 1. A heat current \mathbf{J}_A in a fluid A flows from a heat reservoir B – at a higher temperature T_B – via the fluid A of length L , to a heat reservoir C – at a lower temperature T_C – due to a temperature gradient $(T_B - T_C)/L$.

T_B to the low temperature T_C heat reservoir. It will be assumed that a laminar flow takes place [2].

In order for the system A to return to its original (isolated) equilibrium state, one has to remove the two heat reservoirs, so that the temperature gradient will gradually disappear and the heat current with it.

In books on Non-equilibrium Thermodynamics, e.g. the standard classical book “Non-Equilibrium Thermodynamics” by S.R. De Groot and P. Mazur [3], the main emphasis is that the current must have dissipation, or entropy production, as mentioned above.

A problem then arises in that there seems to be no source to provide the entropy of the equilibrium system, when a non-equilibrium system goes to an equilibrium state. This, since the only source for the equilibrium entropy would be the non-equilibrium entropy production, which disappears – together with the heat current – in the equilibrium state.

The answer to this difficulty is the following: in order to flow in a certain direction, the current \mathbf{J}_A needs an ordering or organization of the fluid particles.

In Non-equilibrium Thermodynamics books, in particular in the book of S.R. De Groot and P. Mazur [3], only the disappearance of the entropy production is mentioned, when the system reaches the equilibrium state, but there is then *no* mechanism is given to provide for the equilibrium entropy.

Therefore, the question arises: what *is* the source of the equilibrium entropy, when the non-equilibrium system has reached the equilibrium state?

The answer is that it has been overlooked, that the heat current \mathbf{J}_A must necessarily have an (inner) ordering or *organization*², since the particles have to flow in a certain direction. This is a direct *physical* consequence of a mathematical representation as a vector, with a magnitude, as well as a direction. Then, when the heat baths are removed and the gradient gradually disappears, the heat current will more and more disintegrate and randomize, losing its organization. When the equilibrium state is reached, a maximum randomization or entropy will have been obtained, as required by Equilibrium Thermodynamics.

Therefore, it is the current’s organization, which disappears when the system reaches equilibrium and then provides the ensuing randomization of the fluid particles

² The organization of the current can be observed a.o. by inserting a dye into the fluid, which will show the streamlines of the organized currents, as shown in [4].

to produce the equilibrium entropy. This implies that the Non-Equilibrium Thermodynamics [3] textbooks, where the current is merely represented *mathematically* by a symbol \mathbf{J} , has in addition a *physical* nature, in that it is an organization of the fluid particles, above and beyond just a mathematical symbol.

When the external forces, which created from an equilibrium system a non-equilibrium system are removed, the temperature gradient as well as the heat current will gradually disintegrate and disappear, when an equilibrium state will be reached. Therefore, it is the loss of the current's organization, which leads to an increasing randomization of the system, and creates the equilibrium system's maximum entropy, in agreement with Equilibrium Thermodynamics.

Thus, one could call the current's organization "antropy", from anti-entropy, in view of the transmutation of the non-equilibrium current organization into the equilibrium entropy.

Alternatively, when a temperature gradient is introduced into a system in equilibrium, a non-equilibrium heat flow will appear, which leads to an organized heat current. The above suggests that it is important to consider, together with the non-equilibrium state, *also* the equilibrium state and not only consider the disappearance of the entropy production of the non-equilibrium state as in [3].

In addition, in Non-Equilibrium Thermodynamics textbooks, as in the standard classical book [3], the current is represented mathematically by a vector, \mathbf{J} , which has an additional important physical aspect, as being *organized*, in order for the fluid particles to flow in a certain direction.

The reason that the current's organization is not mentioned in [3] is that in non-equilibrium thermodynamics textbooks, only the non-equilibrium state itself is considered and the equilibrium state is only mentioned in connection with the disappearance of the entropy production.³

Finally, the difference between mathematics and physics has, in my opinion, nowhere been better characterized than by J.W. Gibbs in a footnote on page 35 of his classical book 1902: "Elementary Principles in Statistical Mechanics" (Yale University Press, 1902), (Dover Publications, New York, 1960). There he says in a footnote: "... Again two attracting particles should be able to do an infinite amount of work in passing from one configuration (which is regarded as possible) to another, is a notion which, although perfectly intelligible in a mathematical formula, is quite foreign to our ordinary conceptions of [ponderable] matter [i.e. to physics]."

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³ This reminds me of my postdoctoral stay with Professor G.E. Uhlenbeck, who occasionally mentioned derogatorily that someone had become an "expert" working in one field only. Although I then aspired just that, later I realized the wisdom of his remark.

Debate. On the transition of a non-equilibrium system to an equilibrium System by E.G.D. Cohen

Comments by H. Qian

When a conservative, Hamiltonian system is in contact with two heat baths with $T_1 > T_2$, there will be a heat flow, passing through the system, from bath 1 to bath 2. The system is in a nonequilibrium state: First follows a time-dependent transient, and eventually settles into a nonequilibrium steady state. The issue Professor Cohen raises is this: when this Hamiltonian system is detached from both baths at time $t = 0$, it is like any other Hamiltonian dynamics with a particular initial conditions in phase space. On the other hand, most people will agree that this system still requires a period of “relaxation” to finally reach its equilibrium state. So what is the source of entropy increase for the transient process for $t > 0$? The answer to this question from standard textbooks is this: the entropy associated with the initial condition is smaller than that associated with the equilibrium state. But how to compute this entropy for a particular Hamiltonian system? There is no ensemble, there is no probability, and there is only a single point moving in phase space. Let us put this more bluntly and consider a pendulum $\ddot{\theta} = -\sin \theta$ with initial value $\theta(0) = \theta_0$ and $\dot{\theta}(0) = \omega_0$. What is the initial entropy, and what is the final (equilibrium) entropy?

The answer to the above question is not as simple as textbooks, which inevitably use an ideal gas that consists of a collection of identical, independent particles as illustration, lead us to believe. In fact, one important thing to remember is this: A thermodynamic state of a mechanical system is not a single point¹ in its phase space, it is actually a state of motion [1]. According to Helmholtz and Boltzmann, it is the entire invariant torus associated with the given initial condition!

Cohen’s thesis is to characterize both the initial and final (equilibrium) states using “current” \mathbf{J} as a key physical observable. The intuition is that its initial value $\mathbf{J}(0)$ should have a non-vanishing value precisely equals that when the system was detached from the two baths, and its final value $\lim_{t \rightarrow \infty} \mathbf{J}(t) = 0$. One of the advantages of using the notion of current is that $\mathbf{J} \neq 0$ can be identified, intuitively, as a kind of “organization”. Thus, it has a lower entropy. The paper does not tell us how to formulate such a \mathbf{J} for a given Hamiltonian system. This problem is at the heart of macroscopic irreversibility. Boltzmann, together with Helmholtz, was able to rigorously introduce a mechanical theory of heat and entropy, and derived the First Law; but was not able to rigorously derive the Second Law from Hamiltonian dynamics alone. Even chaotic motion with mixing is not sufficient to achieve that. One needs dynamics with either many-to-one (endomorphism), or one-to-many (non-deterministic) characteristics [2].

There is a very different, probabilistic approach to this problem: There are actually many different initial conditions all consistent with the same macroscopic, non-equilibrium state at time $t = -\varepsilon$. This provides a natural ensemble of states for $t > 0$.

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Comments by Y. Pommeau

I find the discussion by Hong of Cohen's contribution of outstanding interest. However I have a few disagreement with points raised by both. I believe this does not take into account the work done by Kolmogorov and his school on ergodic problem. The apparent contradiction between irreversibility and formally reversible Lagrangian dynamics is lifted, I believe, when one realizes that there is a Markov partition, and when one can show (as was done by Hopf and Sinai) that such a partition exists for the Lagrangian dynamics of hard spheres. Once this is done, if I understand well those rather deep mathematical results, the system is Bernoulli and has all the properties needed for making an irreversible dynamical system. Somehow, as has been emphasized often by Prigogine, the system is equivalent to a baker's map and show entropy growth. Somehow this property of growing entropy due to the exponential divergence of trajectories is hidden in the definition of the non equilibrium entropy introduced by Boltzmann for dilute gas dynamics. Such a growth of entropy makes sense in the thermodynamic limit only. Said otherwise, by considering instead of a particular trajectory a set of such trajectories one finds that the density of trajectories in phase space tends to the invariant ergodic measure, which I think is the key to the understanding of macroscopic irreversibility.

To come to the contribution of Eddie Cohen, Hong is right when he says that textbooks in statistical physics do not give a clear picture of the problem, but I disagree with his statement that Boltzmann did not derive the second law from Hamiltonian mechanics. I think he derived it for dilute gases from both the Stosszahlansatz and the mechanics of two-body collisions. In the thermodynamic limit this gives a fairly complete proof of second law. Indeed the pendulum is not covered by Boltzmann results because there is no Lyapunov instability of individual trajectories. Lastly, if I understand well, Eddie Cohen says that the dynamical entropy (in the sense of Boltzmann kinetic theory) is at a maximum for local equilibrium, so that any deviation to local equilibrium will decrease this entropy and so put more order in the system. This is correct, but I think it somehow obscured by the attempt to mix in the same paper the production of entropy and the value of the entropy itself. Perhaps it would be interesting to put this on a slightly more concrete basis by considering shock waves: one has the well-known production of entropy across the shock, which does not tell how entropy itself is distributed across the shock, with sometimes a maximum inside, because of the complicated balance between entropy flux and entropy variation by the "ordering of the flux" (namely because of the deviation of the state of maximum entropy).

A last point is that Eddie Cohen assumes implicitly that there is a fair definition of entropy in general nonequilibrium systems. As well known such a definition does not exist outside of the dilute case, where one may associate Boltzmann entropy to the thermodynamical entropy to show that entropy increases. As well known too, the derivation of Boltzmann kinetic theory requires an assumption on the initial conditions, the famous Stosszahlansatz. This is the heart of the matter: indeed such an ansatz implies something about the initial conditions. In a dilute gas it seems reasonable, but there is no known way to extend it to dense systems. In particular, as soon as density increases this ansatz requires to consider (for instance when considering three body collisions) an assumption on the state some time before the present one, since three body collisions may take some time. Even worst, as I showed in my PhD thesis [1], outside of equilibrium there are very long range interactions relying on the propagation of correlations by hydrodynamic modes, and those interactions propagate also on very long times (something that is absent at equilibrium only). Because of this, the initial conditions for a collision depend on the state of the system in a very remote past, particularly in 2D where there is a fundamental divergence of the

kinetic theory. Therefore it seems to me very difficult, to not say impossible to build a fair entropy outside of equilibrium.

References

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Response to the comments of Y. Pomeau, by H. Qian

I completely agree with all the things said in Yves' comments. In fact, the one sentence at the end of my comment, "One needs dynamics with either many-to-one (endomorphism), or one-to-many (non-deterministic) characteristics [2]" is precisely poised for the full discussion of the work of Sinai, and the entire, very successful, Markov partition approach to chaotic dynamics.

There is no doubt that both Boltzmann's original work based his Stosszahlansatz, and Kolmogorov and Sinai's Markov partition provided deep insight into deterministic dynamics. But Boltzmann's approach really added something to the Hamiltonian dynamics, making his equation a stochastic process. In fact, both approaches ultimately succeeded by establishing the "entropy theory" in the stochastic setting. This fact should not be overlooked.

It is also worth mentioning that even chaotic mixing is not enough for H-theorem. One really needs exactness. Certainly Professor Cohen knew all these. I believe the significance of this little piece is, after many years of deep thinking on this subject, the author now clearly recognized the importance of "flux", something many practitioners in the field have neglected, especially in stochastic processes. It is also worth mentioning the beautiful work of Pierre Gaspard on transport phenomena in the chaotic setting "Chaos, Scattering and Statistical Mechanics" (Cambridge Univ. Press, 1998).

General response by E.G.D. Cohen

My paper is mainly a critique of the classical standard book on Non-Equilibrium Thermodynamics, by S.R. de Groot and P. Mazur: "Non-Equilibrium Thermodynamics" in paperback (Dover). In this book, the material has nothing to do with Hamiltonian systems, because there can not be any dissipation in such systems.

The main point is – admittedly with the knowledge of hindsight – that it is "ridiculous" to discuss Non-Equilibrium Thermodynamics *exclusively* from the point of view of the entropy production or dissipation, as its main subject. This, because the entropy production is only a small side effect, when compared with the flowing – and therefore overlooked – *self-organized* currents – which are – in my opinion – by far the most important ingredients in the Non-Equilibrium state of a fluid and their self-organization is – in addition – the source of the equilibrium entropy. In a way, when the system reaches the Equilibrium State, the currents' organization has been transformed (i.e. "randomized") into the (maximum) equilibrium entropy... The – to me – un-understandable thing is, that nobody seems to have noticed before, that 1. not only is the entropy production merely a *small*, but necessary (because of the

Second Law of Thermodynamics) side effect, but 2. the *main* effect are the *flowing* currents, which require an internal ordering or organization, in order to flow in a certain direction. Interestingly enough, De Groot and Mazur do of course mention and use the currents, but merely as *vectors*, i.e. as *mathematical* entities, not as important *physical* quantities. It is therefore the necessary inner ordering or organization of the currents in a Non-Equilibrium system, which also provides the source to the equilibrium entropy, thus making a direct connection, between these two very different states.

I noticed the neglect of the importance of the currents and their organization, because I could not understand where the equilibrium entropy came from, when a fluid in a Non-Equilibrium State goes to an Equilibrium State. Since the Non-Equilibrium entropy production vanishes in the Equilibrium State, there is no obvious source for the equilibrium entropy in the Non-Equilibrium State. Therefore the long overlooked question for me then was: what *is* then the source of the equilibrium entropy, i.e.: where does it come from, when a Non-Equilibrium System goes to Equilibrium?

The answer to the source of the Equilibrium Entropy is therefore that the currents necessarily have a most important – but up until now – overlooked ordering or *self-organization*, in order to be able to flow in a certain direction. In view of the above, when a Non-Equilibrium system goes to an Equilibrium State, the equilibrium (*disordered*) Entropy is obtained from the Non-Equilibrium Current (*ordered*) Organization. This organization will then gradually disappear when the system goes to *equilibrium*, because the current causing *gradients* will then gradually disappear and the currents' organization obviously disappears with this, so that the system increasingly randomizes. Thus, when the system goes to Equilibrium, the system will increasingly randomize due to the increasing disappearance of the currents' organization. This creates then the *maximum* equilibrium entropy, when the equilibrium state is reached, as required by Clausius for a system in Thermal Equilibrium. In a way, it concerns here therefore “an order – disorder” transition.

Alternatively, this also implies that when a system goes from an Equilibrium State to a Non-Equilibrium State, it is the equilibrium (disordered) entropy which transforms into the Non-Equilibrium current's (ordered) organization, a rather unexpected result, I think. This transformation also requires that work has to be done on the equilibrium system, in order to reach the Non-Equilibrium State, so that the energy of the Equilibrium State is a minimum, as is also required by Clausius.

I would say obviously the main attribute of the currents are their flowing, and their inner friction is only a small side effect. In fact, it better be, since if this friction would be strong enough, the current could not flow – the necessarily organized currents – which are, therefore, a small side effect, as an inner friction, i.e. a dissipation or entropy production – i.e. inducing a disorder, like the equilibrium entropy, but physically entirely different in nature, since it is a non-equilibrium effect, which has nothing at all to do with the equilibrium entropy. Its origin is the Second Law of Thermodynamics, which states the impossibility of a *perpetuum mobile* of the second kind, i.e. a machine, which could do work indefinitely, by using *all* the heat from an (infinite) heat reservoir, to do work “*ad infinitum*”.