On the Problem of Defining Local Thermodynamic Equilibrium

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1 Introduction

There are two statements which may come to your mind when reading the title of this paper: "Everybody knows what local thermodynamic equilibrium means", and: "Nobody has ever given a really satisfactory definition of local thermodynamic equilibrium". I can defend both of them under suitable conditions; and I shall do so in the following concentrating mainly on the second one. This article will not give answers, let alone a precise definition of local thermodynamic equilibrium; my aim is to bring the related problems into sharp focus.

The generic case of a macroscopic system is one which requires thermodynamics in its description, but which is not in global equilibrium; any viscous fluid, any elastic medium with internal friction exhibit generation and dissipation of heat. That is, the concepts of heat — and thus thermodynamics — enter necessarily; but global thermodynamic equilibrium can be expected only under special circumstances. There is another line of arguments based on principal grounds: starting from Galilei group theoretic considerations in defining the concept of continuous media one finds that one cannot avoid the notion of internal energy and thus thermodynamics [RSS]. It is to be stressed that we are speaking of thermo*dynamics*, not merely of thermostatics.

Equilibrium relations are well established; and there are relations for non-equilibrium as well, e. g., Fick's law, Fourier's law, Onsager's reciprocity relations. These are successful phenomenological relations akin to the spirit of linear response theory; but they presuppose tacitly that the medium under consideration can be considered as a thermodynamic equilibrium system *locally*, i. e., quantities used to describe systems in thermal equilibrium are assumed to exist at every point, that is, they are now continuous functions of space and time. This is how one would define local thermodynamic equilibrium phenomenologically; and this is not a deep insight, hence my first statement: "Everybody knows what local thermodynamic equilibrium means."

Of course, not every macroscopic system can be considered as a continuous system of that sort; there are many cases where a microscopic view is necessary which takes the particle structure into account. Take as an example the solar photo- and chromosphere above relative cool solar spots governed by strong magnetic fields where rather turbulent motions of particles prevail; there are good arguments that this is not a local thermodynamic equilibrium situation [St].

The question of systems treated microscopically brings us to the following problem: under which circumstances can we extract a continuous media picture from the particle point of view, i. e., under which cirstumstances can we define, and how can we define, the notion of local thermodynamic equilibrium from the viewpoint of Statistical Mechanics.

Equilibrium statistical mechanics is by now a well established theory, also from a mathematically rigorous point of view. The essential idealization involved is the passage to the thermodynamic limit, i. e., to a system of infinitely many particles in an infinite volume but with finite mean density; thereby one is, firstly, freed from problems of boundary effects, and, secondly, able to describe phase transitions in a clear-cut way. It is worthwhile to recall the basic axiom of equilibrium statistical mechanics: *Global equilibrium states are defined by the (classical or quantum) KMS condition.* For finite systems these are nothing but the Gibbs states; for infinite systems the axiom is validated, firstly, by its success in reproducing thermodynamics (or better: thermostatics), and, secondly, by the theorems of Haag, Kastler and Trych-Pohlmeyer [HKT] and of Pusz and Woronowicz [PW]. Stationarity and dynamical stability are minimal requirements for a state to be called an equilibrium state; the first mentioned theorem is a stability theorem stating in essence that these two conditions — apart from technical assumptions — are necessary and sufficient to imply the KMS condition. The second one is a passivity theorem which can be rephrased by saying that it is precisely the KMS states which are distinguished by the second law of thermodynamics in Kelvin's formulation: there are no cyclic processes converting heat into mechanical work if the state of the systems obeys the KMS condition.

Physical intuition tells us that in a closed system of very many particles "most" initial states evolve towards equilibrium under the microdynamical time evolution. This can hold only if the states are not measured down to the last atom, that is, if not all (compatible) microscopic observables are measured. In order to convert the intuition into a theorem one has to specify what equilibrium means, which are the relevant observables,

and, moreover, to define the notion of "most states". This then could replace the above axiom, albeit subject to another axiom that the exceptional states are irrelevant; but no such theorem is known to me.

For non-equilibrium systems the situation is far less clear. In order to arrive at a formulation of similar mathematical rigor we would like to perform the thermodynamic limit, too; but now it has to be done "pointwise", i. e., every macroscopic point, which is actually a macroscopically small volume, has to be considered as an infinite system. This involves a scaling limit. Problems connected to this difficulty have been tackled, but up to now no rigorous definition of local thermodynamic equilibrium has been given; and this is the justification of my second statement in the first paragraph. I shall elaborate on that.

The intuitive idea behind the definition of global equilibrium by the Gibbs states or, in the microcanonical ensemble, via equipartition of probability among the microstates, is that inevitably there are small perturbations not taken into account explicitly in the Hamiltonian, which, in the course of time, lead to a maximally mixed state, the (mean) energy being the only conserved quantity (apart from the particle density and external parameters). These perturbations — "a grain of dust in the system" — act as thermalizing agents. I want to stress that the definition of equilibrium is not a natural outcome of the dynamical laws of mechanics or quantum mechanics; actually it is an additional assumption, a first "hypothesis on thermalization", which goes beyond the dynamical laws. My thesis is that we need another thermalizing hypothesis singling out states exhibiting thermal equilibrium *locally*.

2 Phenomenological considerations

Let us start with a definition:
A system is in local thermodynamic equilibrium at a given time if there is a well-defined temperature $T(x)$ at any macroscopic point x.
The term "well-defined" is meant not only mathematically but physically: the temperature is defined as the parameter governing thermal equilibrium between two systems, i. e., coupling a heat reservoir at temperature $T(x)$ to the system at point x would not change the state of the system. As an additional requirement we demand continuity of $T(x)$ in the interior of the volume under consideration. Furthermore, in order that the concept is of any use, local thermodynamic equilibrium should prevail for at least a finite time interval.

It is not hard to invent necessary conditions for local thermodynamic equilibrium with a microscopic point of view in mind. Consider a continuous system which is to be described hydrothermodynamically. In order to speak of local thermodynamic equilibrium we should be able to exhibit a "macroscopically small" volume V at the "macroscopic point x", i. e., small compared to length scales L on which typical macroscopic quantities change markedly. Furthermore, it is certainly necessary to have "many" particles in V. Finally, the time needed to reach local equilibrium should be small compared to time scales on which macroscopic changes occur.

To make this a bit more precise in the case of a fluid consider a small volume V flowing along with mean velocity $\langle v\rangle$. Define $l := V^{1/3}$ and $L := \left(\langle\nabla v\rangle/\langle v\rangle\right)^{-1}$. L denotes the length scale on which macroscopic velocity changes occur. Our first requirement then reads $l \ll L$ or, equivalently,

$$l\,\langle\nabla v\rangle \ll \langle v\rangle\ .$$

Let ρ be the mass density, m the particle mass, then the second requirement is

$$l \gg \left(\frac{m}{\rho}\right)^{1/3}\ .$$

A lower bound for the relaxation time is given by the mean time t_1 needed for a particle to traverse the volume V which is flowing along with velocity $\langle v\rangle$: if Δv is the mean velocity fluctuation, then $t_1 = l/\Delta v$. The time scale for macroscopic changes can be estimated by the time needed for a particle to traverse the length L: $t_2 := L/\langle v\rangle \approx \langle\nabla v\rangle^{-1}$, which has to be large compared to t_1, consequently,

$$l\,\langle\nabla v\rangle \ll \Delta v\ .$$

This is what I have to say about the definition of local thermodynamic equilibrium on a phenomenological level.

3 The Boltzmann equation

As a step intermediate between the macroscopic description and the full microscopic picture let us consider the example of a system described by the Boltzmann equation. This is an intermediate — mesoscopic — description because it already involves an idealization, e. g. the Boltzmann-Grad limit [Gr] which leads from the full (classical) dynamical equations containing the exact particle interaction to an equation for the one-particle distribution function $f(\vec{x},\vec{v},t)$. The Boltzmann-Grad limit can be interpreted as letting the particle number N go to infinity and simultaneously shrinking the mass m and diameter σ (resp. the range of the interaction) of the particles such that the mass density and the cross section remain finite. The resulting system is to be considered as an ideal gas with no interaction left apart from an (idealized) hard core interaction.

Let us note that only in this case of vanishing interaction is the description by the one-particle distribution function sufficient: even for thermodynamics, where we do not need the full information about the microscopic state, we would in general get wrong results when calculating the density of the potential energy with the help of $f(\vec{x}_1,\vec{v}_1,t)f(\vec{x}_2,\vec{v}_2,t)$ instead of the correct two-particle distribution function which need not factorize.

There is a special class of solutions: Hilbert's "normal" solutions [Hi] which are defined via their method of construction by a series expansion.

Their first moments give the mass density ρ, the mean velocity $\vec{u}$ and the density of the kinetic energy ε_{kin}:

$$\begin{aligned} \rho(\vec{x},t) &= \rho_0 \int f(\vec{x},\vec{v},t)\,d^3v\ , \\ u_k(\vec{x},t) &= \rho_0 \int v_k f(\vec{x},\vec{v},t)\,d^3v\ ,\ k=1,2,3\ , \\ \varepsilon_{\text{kin}}(\vec{x},t) &= \rho_0 \int |\vec{v}|^2 f(\vec{x},\vec{v},t)\,d^3v\ , \end{aligned}$$

the constant ρ_0 is the global mass density. Conversely, any normal solution is completely characterized by its first moments at a fixed initial time. That is, the above quantities provide a complete description of our system, they are determined by their initial values alone, and are sufficient to recover $f(\vec{x},\vec{v},t)$. This property is not shared by non-normal solutions.

Let us define the internal energy density

$$\varepsilon_{\text{int}}(\vec{x},t) := \varepsilon_{\text{kin}}(\vec{x},t) - |\vec{u}(\vec{x},t)|^2/2\rho(\vec{x},t)\ ;$$

it is then in the spirit of our idealization — the Boltzmann gas is an ideal gas — to put $\varepsilon_{\text{int}}(\vec{x},t)$ proportional to the temperature T at the point $\vec{x}$ at time t. We may replace $\varepsilon_{\text{kin}}(\vec{x},t)$ by $T(\vec{x},t)$ thus arriving at a hydrothermal description of our system with a well-defined temperature at any macroscopic point, i. e., exhibiting local thermodynamic equilibrium.

Some remarks are in order.

1. The above characterization of normal solutions as local thermodynamic equilibrium states hinges on the proportionality of ε_{int} and T. But this can be considered a rather arbitrary definition of T taken over from thermostatics. Remember that the temperature is originally defined as parameter governing thermal equilibrium between two systems; there is no such justification like that here. An ideal gas in global thermal equilibrium exhibits a Maxwellian velocity distribution; but this is not the case for Hilbert's solutions, it holds true only in lowest approximation.
2. What is the thermalizing hypothesis behind the above definition of local thermodynamic equilibrium? The Boltzmann equation implies Boltzmann's H-Theorem, i. e., evolution towards global equilibrium for all solutions (and not only for the normal ones). Thus time reversal invariance is broken. The relevant assumption for that is hidden in the derivation of the Boltzmann equation: the assumption of "molecular chaos", i. e., the assumption that the velocities of colliding particles are statistically independent before the collision. Of course, this is not the case immediately after the collision; but it is assumed that statistical independence is restored by the "grain of dust" before the next collision occurs. There is a second part of the thermalizing hypothesis: the assumption that we have to consider normal solutions, and that $\varepsilon_{\text{int}} \propto T$.
3. The Boltzmann equation is of course not the most general case of a

classical mesoscopic equation (or set of equations). In general, one has a hierarchy of equations for the n-particle distribution functions, $n = 1, \ldots, \infty$. But in that case, as in the case of general Boltzmann solutions, the connection to thermohydrodynamics is by no means obvious. Furthermore, one should start from quantum systems on the microscopic level, as is done in a paper of Narnhofer and Sewell [NS]; cf. the comments on that paper in Section 5.

4 The scaling limit

Let us now start from a general microscopic point of view. We have to keep in mind that defining local thermodynamic equilibrium means defining a macroscopic time evolution, too, starting from the microscopic interaction. Global thermal equilibrium states are time invariant ones, and the KMS condition is defined relative to the microscopic time evolution. But states exhibiting local thermodynamic equilibrium will, in general, not be stationary on a macroscopic scale although we want them to be locally KMS and hence time invariant microscopically.

The following gives an indication of the difficulties we have to face: defining a macroscopic time evolution may come close to solving the problem of evolution towards equilibrium of fairly arbitrary initial states. Up to now only the *return* to equilibrium has been treated satisfactorily, where the initial states are locally disturbed equilibium states.

Starting from a microscopic picture requires a twofold idealization: taking the thermodynamic limit *locally* (i. e., "many" particles in a small volume dV), and at the same time shrinking the (macroscopically) small volume to a point in order to define the local fields of velocities, pressure, temperature etc. This can actually be achieved by performing a scaling limit; a possible scheme which, at the same time, yields a macroscopic time evolution by means of a simultaneaous time scaling will be described in the following.

Let the macroscopic system be contained in a region $\Gamma \subset \mathbb{R}^3$; for brevity we shall write $x \in \Gamma$ instead of $\vec{x} \in \Gamma$. We start — using the language of quantum theory — with a quasi-local algebra of observables $\mathcal{A}$ generated by a net $\{\mathcal{A}(\Lambda)\}_{\Lambda \subset \mathbb{R}^3}$, $\mathcal{A} = \overline{\bigcup \mathcal{A}(\Lambda)}$, a net $\{H_\Lambda\}$ of corresponding Hamiltonians, and a net $\{\omega_\Lambda\}$ of states over $\mathcal{A}(\Lambda)$. We denote the states over $\mathcal{A}$ by $\mathcal{S}(\mathcal{A})$. Our aims are: 1) to "attach" a copy of $\mathcal{A}$ to every $x \in \Gamma$ (corresponding to the local infinite system); 2) to single out suitable nets $\{\omega_\Lambda\}$ defining "macroscopic" states, where a macroscopic state is a set $\{\omega_x \in \mathcal{S}(\mathcal{A})\}_{x \in \Gamma}$ of states over $\mathcal{A}$ attached to the points of Γ, describing the local properties; 3) to define the dynamics of the macroscopic states based on the microscopic interaction given by a net of Hamiltonians $\{H_\Lambda\}$. The region Γ will be considered finite in order to leave open the possibility of introducing macroscopic boundary conditions.

Let us introduce a scaling parameter κ which will tend to infinity, and scale Γ by a factor of κ in order to "gain a microscopic point of view": $\Lambda_\kappa := \kappa\Gamma$; we assume that the origin of the macroscopic coordinate system is in Γ. The "microscopic" coordinates will be denoted by $\xi = \kappa x$. Now let us consider an arbitrary strictly local observable $A \in \mathcal{A}_{\Lambda_0}$, Λ_0 fixed. For sufficiently large κ, and x in the interior of Γ, Λ_0 as well as the translated region $\Lambda_0 + \kappa x$ are contained in Λ_κ; the set of space translated observables $\{\sigma_{\kappa x}(A) \in \mathcal{A}(\Lambda_\kappa); \kappa \in \mathbb{R}^+\}$ is considered as representing the copy of A attached to $x \in \Gamma$.

We now require that the sequence $\omega_\kappa \equiv \omega_{\Lambda_\kappa}$ be chosen such that

$$\lim_{\kappa\to\infty} \omega_\kappa(\sigma_{\kappa x}(A)) =: \omega_x(A) \tag{1}$$

exists for all strictly local A and all $x \in \Gamma$. By continuity, ω_x can be extended to a state over $\mathcal{A}$. The set $\{\omega_x\}_{x\in\Gamma}$ is said to be a macroscopic state; and ω_y is the local state corresponding to the macroscopic point $y \in \Gamma$.

It is not hard to construct fairly arbitrary macroscopic states. The construction is roughly as follows. Start from a given set $\{\omega_x\}$ of local states depending continuously on x. Divide Λ_κ into disjoint subsets $\Lambda_{\kappa l}$ with centers $\xi_{\kappa l} = \kappa x_{\kappa l}$ making sure that the $x_{\kappa l}$ form a dense set of Γ as $\kappa \to \infty$ while the subsets $\Lambda_{\kappa l}$ increase to $\mathbb{R}^3$. Define ω_κ by gluing together the states $\omega_{x_{\kappa l}}$ belonging to the centers of the subsets of Λ_κ. Finally, take the limit $\kappa \to \infty$. We omit the subtleties of the construction; but we claim that the resulting macroscopic state has the set $\{\omega_x\}$ as local states. In this way we may construct a macroscopic state of continuously varying local inverse temperature $\beta(x)$ by choosing the states ω_x as $\beta(x)$-KMS states.

Of course, in order to do so we need a well-defined microscopic time evolution. For that end let us assume that the automorphisms α_t^Λ of $\mathcal{A}_\Lambda$, given by

$$\alpha_t^\Lambda(A) = e^{itH_\Lambda} A e^{-itH_\Lambda},$$

define a limiting automorphism α_t of $\mathcal{A}$ or at least a map α_t^* of a suitable subset of $\mathcal{S}(\mathcal{A})$ describing the time evolution of the microscopic system in the Heisenberg or in the Schrödinger picture. The concept of a KMS state is defined in the Schrödinger picture as well [Ro], but let us stick to the Heisenberg picture for simplicity.

The crucial point in this scheme is the definition of the time evolution of the *macroscopic* states. If a disturbance of the microscopic system spreads with a finite velocity one cannot expect any change of ω_x in time induced by the properties of the system at neighbouring points unless time is scaled, too. For the sake of generality let us introduce a time scaling factor $\gamma = \gamma(\kappa)$, $\lim_{\kappa\to\infty} \gamma(\kappa) = \infty$ and write $\tau = \gamma t$, where τ is now the microscopic time. In the spirit of equation (1) we would like to define $\omega_{t,x}$ by

$$\omega_{t,x}(A) := \lim_{\kappa\to\infty} \omega_\kappa \circ \alpha_{\gamma t}^{\Lambda_\kappa}(\sigma_{\kappa x}(A)) \,, \tag{2}$$

provided the limit exists. Its existence is to be considered as an additional requirement on a net $\{\omega_\kappa\}$ defining a macroscopic state.

There is a case for taking $\gamma(\kappa) = \kappa^2$ (van Hove limit) [vH, Oj]; this choice corresponds to the fact that in Brownian motion the mean distance travelled in time t is proportional to $\sqrt{t}$. On the other hand, if there is a finite propagation velocity of a microscopic perturbation (which is the case for lattice systems under fairly general assumptions [BR, Thm. 6.2.11]) one has to choose $\gamma(\kappa) \propto \kappa$ in order to arrive at finite macroscopic propagation velocities. This choice can be justified in still another way:
The requirement of Galilei invariance on the macroscopic as well as on the microscopic scale forces $\gamma = \kappa$.
This follows rather easily by consideration of the transformation properties of macroscopic quantities $f(x,t)$ given by limits of microscopic quantities which might depend on micro-states ω_κ and one or more observables A_κ:

$$f(x,t) = \lim_{\kappa} F_\kappa(\omega_\kappa, A_\kappa; \kappa x, \gamma(\kappa)t)$$

(the dependence of ω_κ and A_κ on κ is assumed to be only through the size of the micro-system considered, they should be the "same" for all κ, $\{\omega_\kappa\}$ forming a macro-state, and $A_\kappa \to A$); applying Galilei boosts to the macroscopic variables (x,t) on the one hand, and to the microscopic variables $(\xi = \kappa x, \tau = \gamma(\kappa)t)$ on the other hand, one finds that necessarily $\gamma(\kappa) \propto \kappa$. Of course, one may doubt that there is a cogent reason for assuming microscopic invariance: all frames of reference which can be realized in the laboratory are connected by *macroscopic* Galilei transformations.

The hard task is not to invent a scheme as the one sketched above, but to prove the existence of the macroscopic time evolution. I know of only two extreme cases where it has been done: the first one is the trivial case of a free Fermi gas [FR], the second one is an inhomogeneous mean field model [DRW]. But let us assume for a moment that this task has been performed. Then the scaling limit allows the definition of local thermal quantities, and of local thermodynamic equilibrium: for the microscopic system attached to a point x we have the microscopic time evolution given by α_t, and we can ask whether ω_x is a $\beta(x)$-KMS state, i. e., whether the temperature at point x is given by $1/k\beta(x)$, try to compute its entropy density, etc.; any such macroscopic state $\{\omega_x\}$ is then to be called a local thermodynamic equilibrium state.

But this is too naïve a view!

Thesis: *Thermodynamics necessitates two "hypotheses on thermalization": a first one to describe global equilibrium, i. e., to single out a set of states which are to be interpreted as equilibrium states; and a second one in order to enforce* local *equilibrium.*

Note that this goes beyond the microscopic picture.

To see that another hypothesis is needed for local thermodynamic equilibrium one may take a look at those two models for which the macroscopic time evolution is known to exist. The mean field model is definitely not trivial, but it suffers from the same defect as the first one: starting from an initial macroscopic state with well-defined local temperature $\beta(x)$, which can be constructed, one ends up — after arbitrarily short macroscopic times — with a state which is no longer locally KMS. This is to be expected in the first model because there is no interaction; it is to be expected of the second model, too: here we have to take $\gamma = 1$, i. e., time is not scaled at all because "mean field interaction" implies infinitely long range interaction, the velocity of spreading of a disturbance is infinite; and this means an immediate destruction of local equilibrium due to the effects of different temperatures at different points.

Similar results are to be expected in more realistic models (for which the above scheme is very hard to implement), hence the requirement of a "thermalizing agent", cf. the molecular chaos hypothesis in the case of the Boltzmann equation.

For the general case one might think of introducing an averaging over microscopic times together with the limiting procedure; this is suggested by a paper of Ojima [Oj] on entropy production. A second possibility would be to adopt the ideas of information thermodynamics of finite volume systems [Rob] to the infinite case. But at the moment these are only vague ideas which will not be followed here.

5 Related papers

There are many papers related to our topic; but this is not the place to review them all. I want to mention only a few ones dealing with nonequilibrium thermodynamics, in order to point out where or how a definition of local thermodynamic equilibrium has been circumvented. I hasten to stress that this is a highly subjective random selection.

The first paper I want to cite is the work of Davies [Da] treating a model for heat conduction. Here heat baths are coupled to every point of the system, their temperatures are to be adjusted according to the interaction. But this means introducing local thermodynamic equilibrium by hand.

As a representative of papers deriving classical macroscopic, or mesoscopic, equations — possibly showing irreversibility — from microscopic ones let me cite a paper by Narnhofer and Sewell [NS] on "Vlasov hydrodynamics of a quantum mechanical model". They derive the Vlasov hierarchy from the microscopic quantum dynamics by means of a "hydrolocal" limit. But in that stage the concept of local thermodynamic equilibrium does not enter. The set of Vlasov equations describe classical correlation functions on a mesoscopic level comparable to the Boltzmann equation, but in greater generality. Another effort is needed to derive macroscopic hydrothermal equations from these correlation functions. One important result of this paper is a theorem stating that the Vlasov dynamics respects "molecular chaos": once the correlation functions factorize as time $t = 0$, they do so at all times. So it seems that this hypothesis is an important part of a thermalizing hypothesis in this case.

Sewell wrote a series of papers [Se1, Se2, Se3] determining restrictions imposed on macroscopic phenomenological laws by microphysics. A lot is achieved by that method; but due to the assumption of the very existence of the macroscopic laws the question of the definition of local thermodynamic equilibrium could be avoided. The last paper contains a nice model, a heavy quantum particle coupled to an infinite chain of small particles, which, in an appropriate limit, yields a classical equation of motion with a frictional force for the massive particle; i. e., the particle tends to the (trivial) equilibrium state of being at rest. But, of course, *local* thermodynamic equilibrium is trivial here.

Verbeure and collaborators have succeeded in deriving quantum central limit theorems [GVV1, GVV2, GVV3] which can be applied in the study of fluctuations. This has been done in a paper by Verbeure and Zagrebnov [VZ]. They showed the existence of a macroscopic limiting algebra of fluctuations. But this is not a macroscopic dynamics in the sense sketched above. First of all, it refers to an equilibrium situation, and furthermore, the resulting macroscopic algebra of fluctuations is dependent on the state underlying the construction.

6 Conclusion

Our conclusion can be kept very short: whatever has been done, a second thermalizing hypothesis is still missing.

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