Alternative point of view on microcanonical temperatures and the direction of heat flows

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Abstract

Statistical mechanics explains many features of thermodynamics in the thermodynamic limit. The aim of quantum thermodynamics is extending the use of thermodynamic concepts to finite systems that are not well approximated by such a limit condition. As pointed out by some authors, under very common assumptions, the temperature parameter of the microcanonical equilibrium seems to be problematic and not predictive of the direction of heat flows. In this paper we give an alternative point of view on this subject, giving a reasonable definition of contact and showing that accepting it there are no more than two values of microcanonical temperature having such a desirable property.

1 Introduction

The problem faced by statistical mechanics is reproducing the thermodynamics' phenomena by means of a mechanical theory of particles. The quantum mixtures representing a thermal state are characterized by a temperature parameter that must correspond to the one of thermodynamics.

This old problem is reasonably solved for macroscopic systems by much time. The situation is the opposite when treating too small finite systems, for which the thermodynamic limit is not a good approximation. Here the definition of temperature and what we can use it for are still topic of debate [1]. In [2, 3] it is suggested that neither the Gibbs nor the Boltzmann microcanonical temperature can be used to establish the direction of heat flows during contacts between bodies: for the microcanonical equilibrium the inverse of the temperature can only have the property of being an integrating factor for reversible heat exchanges. Their argument is based on the fact that, in general, these microcanonical temperatures cannot always identify the state of a system.

In this paper we give an alternative point of view on this specific subject: we approach the concept of temperature by requiring that it can be used, as in thermodynamics, to predict the direction of heat flows. A key concept here is the notion of contact between two systems, that as the definition of work and heat, is matter of convention: we propose a reasonable definition of temporary contact and we show that non-passive states [4] having not maximal energy cannot be associated with temperature values predictive of the heat flow direction. As a particular case we note that the microcanonical ensemble displays a maximum of two temperature values for which such a direction can be established.

2 Definitions and assumptions

The inclusive mean value interpretation of work is widely used, but it is not the only one considered in literature. Other interpretations of work, such as two-measures schemes [5], are not strictly equivalent to the former, that is the one we consider in this paper.

An important concept is the one of "contact" between systems, that in thermodynamics appears as a primitive operation: here we want to provide a corresponding quantum-mechanical definition.

2.1 Work and heat

Let us assume that the dynamics of a system S coupled with an environment E are evolving through the Liouville equation

$$\left(\frac{d}{dt}\hat{\rho}_{SE}\right)(t) = \frac{1}{i\hbar}\left[\hat{H}_{SE}(t),\, \hat{\rho}_{SE}(t)\right] \tag{1}$$

with an Hamiltonian of the form

$$\hat{H}_{SE}(t) = \hat{H}_S(t) + \hat{H}_E + \hat{V}_{SE}. \tag{2}$$

The mean inclusive work done on the system S from time t_1 to time t_2 is defined as

$$W_S(t_2, t_1) := \int_{t_1}^{t_2} dt\ \mathrm{Tr}\left\{\left(\frac{d}{dt}\hat{H}_S\right)(t)\hat{\rho}_S(t)\right\}, \tag{3}$$

corresponding to the internal energy variation of SE $E_{SE}(t_2) - E_{SE}(t_1) = W(t_2, t_1)$. The heat absorbed by S is then defined as

$$Q_S(t_2, t_1) := \Delta E_S(t_2, t_1) - W_S(t_2, t_1). \tag{4}$$

It is known that such definitions are somewhat ambiguous because of a gauge freedom conserving the dynamics but affecting the values of work [5]. We refer to a temporary perturbation from t_1 to t_2 as a potential $\hat{V}(t)$ such that

$$\hat{V}(t_1) = \hat{V}(t_2) = 0. \tag{5}$$

If we assume that the equation (1) holds for any possible $\hat{\rho}_{SE}(t)$ and we consider only Hamiltonians of the form

$$\hat{H}_{SE}(t) = \hat{H}_{SE}(t_1) + \hat{V}(t) \tag{6}$$

where $\hat{V}(t)$ is a temporary perturbation from t_1 to t_2, then it can be shown (see Appendix A for a custom proof) that the work done on the system SE during the interval of time $[t_1, t_2]$ is gauge independent.

2.2 A concept of contact

In thermodynamics a temporary contact between two bodies A and B is a mechanical operation that one can perform at will. In general this is characterized by an interaction with an auxiliary system E (e.g. experimenter) whose action is simply mechanical, that is its own contact with the subjects of the experiment results in a heat transfer that is negligible at all times. At the initial and final time, the two systems are decoupled and the work done in the whole process is null.

Let us give to this process a microscopic equivalent conforming with the notions of heat and work we have taken. We assume that the state of AB to be evolving by means of the time-dependent Liouville equation

$$\left(\frac{d}{dt}\hat{\rho}_{AB}\right) = \frac{1}{i\hbar}\left[\hat{H}_{AB}(t),\, \hat{\rho}_{AB}(t)\right] \tag{7}$$

where

$$\hat{H}_{AB}(t) = \hat{H}_A + \hat{H}_B + \hat{V}_{AB}(t): \tag{8}$$

in this way, by definition, the system AB is not going to exchange any heat at any time, whatever the Hamiltonian gauge. We identify a temporary contact from t_1 to t_2 for $\hat{\rho}_{AB}$ as a temporary perturbation $\hat{V}_{AB}$ from t_1 to t_2 satisfying

$$W_{AB}(t_2, t_1) = 0, \tag{9}$$

for the dynamics of that specific $\hat{\rho}_{AB}(t)$.

This viewpoint is formally equivalent to the idea of a quantum heat engine operating between two bodies and performing a cycle where the total extracted work is zero.

3 Temperatures and prediction of heat direction

In this section we address the temperature concept as a parameter used to predict the direction of heat flows in temporary contacts. Enforcing such a property we filter out quantum states that surely cannot be associated to a predictive temperature parameter. At last, with this in mind, we look at the case of the microcanonical ensemble.

3.1 Requirements

We want to consider two basic properties that the temperature concept has in thermodynamics.

1. to any body in thermal equilibrium we can associate a temperature

2. knowing the temperatures of two bodies before a temporary contact allows us to predict where the heat will not flow

Translated by quantum mechanical means they can be stated as:

1. Given a system A we name a subset its reduced quantum states as $L(A)$; there is a temperature function associating them and the Hamiltonian to a temperature value:

   $$T = T(\hat{H}_A, \hat{\rho}_A), \tag{10}$$

   with $\hat{\rho}_A \in L(A)$.

   Let $L(A, T)$ be the subset of $L(A)$ whose states have a certain temperature T.

2. There is a function $F : (T_A, T_B) \to \{-1, 1\}$ such that for all initial $\hat{\rho}_A \in L(A, T_A)$ and $\hat{\rho}_B \in L(B, T_B)$

   $$\Delta E_B \cdot F(T_A, T_B) \geq 0 \tag{11}$$

   for each transformation of the initial state $\hat{\rho}_{AB}$ caused by a temporary contact.

3. If $T_A = T_B$ it also holds

   $$\Delta E_B = 0 \tag{12}$$

   after each contact.

In the following we show that, in order to satisfy such properties, the set $L(A)$ of a certain system A cannot contain many states of microcanonical equilibrium.

3.2 Filtering out quantum states which are not associated with a predictive temperature

Let $\hat{H}$ be the Hamiltonian of a certain isolated system and $\hat{\rho}$ its current state: the variation of internal energy after a unitary transformation $\hat{Q}$ is

$$\Delta E(\hat{\rho}, \hat{Q}) := \operatorname{Tr}\left\{\hat{H}\hat{Q}\hat{\rho}\hat{Q}^\dagger\right\} - \operatorname{Tr}\left\{\hat{H}\hat{\rho}\right\}. \tag{13}$$

Let

$$\xi(\hat{\rho}) = \left\{E(\hat{\rho}, \hat{Q}) \text{ with } \hat{Q} \text{ unitary}\right\}. \tag{14}$$

The idea starts from the concept of ergotropy [6]: if the quantum state of a certain system is not passive there is at least a unitary transformation, always obtainable through a temporary perturbation, extracting some positive work. In our language the ergotropy is

$$\operatorname{Erg}(\hat{\rho}) \equiv -\inf\, \xi(\hat{\rho}). \tag{15}$$

We define an analogous quantity

$$\operatorname{AntiErg}(\hat{\rho}) := \sup\, \xi(\hat{\rho}), \tag{16}$$

that is the maximum positive work that we can do on a system by means by unitary transforming its quantum state. It is intuitive (Appendix B for a proof) that a set of temporary perturbation exists by means of which we can give an arbitrary amount of energy to a system between $-\operatorname{Erg}(\hat{\rho})$ and $\operatorname{AntiErg}(\hat{\rho})$, or more precisely

$$[-\operatorname{Erg}(\hat{\rho}), \operatorname{AntiErg}(\hat{\rho})) \subseteq \xi(\hat{\rho}). \tag{17}$$

We refer to a quantum state such that $\operatorname{Erg}(\hat{\rho}) \neq 0$ and $\operatorname{AntiErg}(\hat{\rho}) \neq 0$ as an intermediate state. Let us consider now the system AB with $A = B$ and assume that $\hat{\rho}_A, \hat{\rho}_B \in L(A)$ are both intermediate. There is a conveniently small energy ϵ such that we can give or extract it from both A and B. We choose to give to A a small amount of energy ϵ and to B a small amount of energy

$-\epsilon$. These two temporary perturbation have as a whole the effect of conserving the total energy of AB, so together they are a temporary contact. The same operation done with ϵ of inverse sign can be done, for the same reason, with a temporary contact, this one leading instead to an opposite heat flow direction: we conclude that $\hat{\rho}_A$ and $\hat{\rho}_B$ cannot be both in $L(A)$ (the second property is not satisfied). Setting $\hat{\rho}_A = \hat{\rho}_B$ we get that $\hat{\rho}_A \notin L(A)$ (the third property is not satisfied).

3.3 The case of the microcanonical ensemble

In the microcanonical ensemble the states are identified by the exact value of the energy of the system under consideration. The microcanonical density matrices can be written as

$$\hat{\rho}_{\text{micro}}(E) = \frac{1}{D(E)} \sum_k \delta(E - E_k)|k\rangle\langle k| \tag{18}$$

with

$$D(E) = \sum_k \delta(E - E_k). \tag{19}$$

We note that for any system A in microcanonical equilibrium

- there is only one passive microcanonical density matrix. It corresponds to the ground state
- if there was a maximal energy there would be only one maximal state
- the other microcanonical states are all intermediate

This means that $L(A)$ would not contain more than two microcanonical states, allowing the existence of two temperature values at maximum giving information of the heat flow direction.

4 Conclusion

Under the mean inclusive definition work we have given a possible reasonable definition of contact between two systems. Starting from these assumptions we got that the prediction of the heat flow direction can be achieved only for passive or maximal energy states.

With the proposed definition of temporary contact, the thermal state has to be passive or with maximal energy, at least for the purpose of inferring where the heat will not surely go.

The argument we have given exploits the generality of such a definition of contact and a possible criticism indeed may be if we had included in it transformations that should not be regarded as temporary contacts: one could, as an example, require the interaction between two systems being direct and mixing the relative subspaces.

Accepting our definition gives another point of view on the inability of the microcanonical temperature in telling the heat direction, that becomes predictable only for the ground state and for the maximum energy state, if existing.

A Workaround to the gauge freedom problem

Consider a system whose Hamiltonian can be changed in time through some controllable parameters and evolving with the a Liouville equation of the kind

$$\left(\frac{d}{dt}\hat{\rho}\right)(t) = \frac{1}{i\hbar}\left[H(t),\, \hat{\rho}(t)\right]. \tag{20}$$

The mean-value definition of the work done during an interval of time is

$$W(t_2, t_1) = \int_{t_1}^{t_2} dt' \, \mathrm{Tr}\left\{\left(\frac{d}{dt}\hat{H}\right)(t')\hat{\rho}(t')\right\}. \tag{21}$$

The choice of the time-dependent Hamiltonian $\hat{H}(t)$ is not unique, there different producing the same dynamics of (20). The problem is that these ones lead to different work values: substituting $\hat{H}$ with

$$\hat{H}'(t) = \hat{H}(t) + \hat{M}(t) \tag{22}$$

where $\hat{M}(t)$ is such that

$$\left[\hat{M}(t),\, \hat{\rho}(t)\right] = 0, \tag{23}$$

then because

$$\mathrm{Tr}\left\{\hat{M}(t)\left(\frac{d}{dt}\hat{\rho}\right)(t)\right\} = \left(\frac{d}{dt}\hat{M}\hat{\rho}\right)(t), \tag{24}$$

we get

$$\begin{aligned} W'(t_2, t_1) = \quad & W(t_2, t_1) \\ & + \mathrm{Tr}\left\{\hat{M}(t_2)\hat{\rho}(t_2)\right\} \\ & - \mathrm{Tr}\left\{\hat{M}(t_1)\hat{\rho}(t_1)\right\} \end{aligned}. \tag{25}$$

This is the gauge freedom problem: while it is not affecting the dynamics, this choice changes the value of work.

Theorem 1. *Let $\hat{M}$ be Hermitian, if $\left[\hat{M},\, \hat{\rho}\right] = 0 \ \forall\ \hat{\rho}$, then it is $\hat{M} \propto \hat{I}$.*

Proof. Let $\{|j\rangle\}$ be a complete set of eigenvectors of $\hat{M}$ and $\{m_j\}$ the corresponding eigenvalues. Consider the density matrix

$$\hat{\rho}_{ij} = \frac{1}{2}\left(|i\rangle\langle i| + |j\rangle\langle i| + |i\rangle\langle j| + |j\rangle\langle j|\right), \tag{26}$$

it holds

$$\left[\hat{M},\, \hat{\rho}_{ij}\right] = \frac{1}{2}(m_i - m_j)\left(|i\rangle\langle j| - |j\rangle\langle i|\right), \tag{27}$$

thus for all i, j

$$\left[\hat{M},\, \hat{\rho}_{ij}\right] = 0 \ \Leftrightarrow\ m_i = m_j. \tag{28}$$

Because $\forall\ i, j \ \ m_i = m_j$, it is $\hat{M} \propto \hat{I}$. ∎

Let $\hat{U}(t, t_1)$ be the evolution operator from t_1 to t associated to the equation (20). By the (23) we have

$$\begin{aligned} &\hat{U}^\dagger(t,t_1)\left[\hat{M}(t),\,\hat{\rho}(t)\right]\hat{U}(t,t_1) \\ &=\left[\hat{U}(t,t_1)\hat{M}(t)\hat{U}^\dagger(t,t_1),\,\hat{\rho}(t_1)\right]=0 \end{aligned} . \tag{29}$$

If we assume the equation (20) to be valid for all possible initial states $\hat{\rho}(t_1)$ then we have

$$\hat{U}^\dagger(t,t_1)\hat{M}(t)\hat{U}(t,t_1) \propto \hat{I}, \tag{30}$$

meaning that the only valid gauges are of the form

$$\hat{M}(t) = f(t)\hat{I} \tag{31}$$

and the gauge problem can be solved by considering valid the values of work only concerning cyclic transformations of the Hamiltonian $\hat{H}(t)$, condition imposing $f(t_2) = f(t_1)$ and then $\mathrm{Tr}\left\{\hat{M}(t_2)\hat{\rho}(t_2)\right\} = \mathrm{Tr}\left\{\hat{M}(t_1)\hat{\rho}(t_1)\right\}$.

B Valid work values

Theorem 2. *[6] Let the states of a system be evolving with a Liouville equation*

$$\left(\frac{d}{dt}\hat{\rho}\right)(t) = \frac{1}{i\hbar}\left[\hat{H}(t),\,\hat{\rho}(t)\right] \tag{32}$$

with

$$\hat{H}(t) = \hat{H} + \hat{V}(t). \tag{33}$$

Let $\hat{Q}$ be an unitary operator, then there is a temporary perturbation $\hat{V}(t)$ from t_1 to t_2 inducing an evolution $U(t_2, t_1) \equiv \hat{Q}$.

Lemma 1. *If $\hat{Q}$ is an unitary operator, then $[0, \Delta E(\hat{\rho}, \hat{Q})] \subseteq \xi(\hat{\rho})$.*

Proof. Let the eigen-decomposition of $\hat{Q}$ be

$$\hat{Q} = \sum_k \exp\left(i\theta_k\right)|k\rangle\langle k|, \tag{34}$$

we can define

$$\hat{M}(\eta, \hat{Q}) := \sum_k \exp\left(i\theta_k\eta\right)|k\rangle\langle k|. \tag{35}$$

The function

$$f(\eta) = \Delta E(\hat{\rho}, \hat{M}(\eta, \hat{Q})) \tag{36}$$

is continuous and such that $f([0, 1]) \equiv [0, \Delta E(\hat{\rho}, \hat{Q})]$. Being the $\hat{M}(\eta, \hat{Q})$ unitary, such $f(\eta)$ values are in $\xi(\hat{\rho})$. □

Theorem 3. *It holds*

$$[\inf\ \xi(\hat{\rho}), \sup\ \xi(\hat{\rho})) \subseteq \xi(\hat{\rho})$$

Proof. Let $\hat{Q}_{\text{pass}}$ be a unitary operator transforming the $\hat{\rho}$ into a passive state. Let $\hat{Q}_k$ be a sequence of unitary operators such that

$$\lim_{k\to\infty} \Delta E(\hat{\rho}, \hat{Q}_k) = \sup\ \xi(\hat{\rho}). \tag{37}$$

For the previous lemma

$$[\Delta E(\hat{\rho}, \hat{Q}_{\text{pass}}), 0] \equiv [\inf\ \xi(\hat{\rho}), 0] \subseteq \xi(\hat{\rho})$$

and for each k

$$[0, \Delta E(\hat{\rho}, \hat{Q}_k)] \subseteq \xi(\hat{\rho})$$

from which the thesis follows. □

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