Determinaton of Nonequilibrium Temperature and Pressure using Clausius Equality in a State with Memory: A Simple Model Calculation

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Abstract

Use of the extended definition of heat $dQ = d_e Q + d_i Q$ converts the Clausius inequality $dS \geq d_e Q / T_0$ into the Clausius equality $dS = dQ / T$ involving the nonequilibrium temperature $T$ of the system having the conventional interpretation that heat flows from hot to cold. The equality is applied to the exact nonequilibrium quantum evolution of a 1-dimensional ideal gas free expansion. In a first ever calculation of its kind in an expansion which retains the memory of initial state, we determine the nonequilibrium temperature $T$ and pressure $P$, which are then compared with the ratio $P / T$ obtained by an independent method to show the consistency of the nonequilibrium formulation. We find that the quantum evolution by itself cannot eliminate the memory effect; hence, it cannot thermalize the system.

There seems to be a lot of confusion about the meaning of temperature, pressure, etc. in nonequilibrium thermodynamics [1–4], where different definitions lead to different results. In contrast, the meaning of temperature in equilibrium thermodynamics as $T = dQ / dS$ has no such problem, even though Planck [5] had already suggested that it should be defined for nonequilibrium states just as entropy is defined. The temperature was apparently first introduced by Landau [6] for partial set of the degrees of freedom. Consider a system $\Sigma$ (in a medium $\Xi$, which is always taken to be in equilibrium at temperature $T_0$, pressure $P_0$, etc.) that was initially in an equilibrium state $A_{\Sigma, eq}$; its equilibrium entropy $S_{\Sigma, eq}(T_0, P_0)$ can also be written as $S_{\Sigma, eq}(E_i, V_i)$, where $E_i, V_i$ are the energy and volume of the system and the suffix $i$ denotes the initial state. If $\Sigma$ is now isolated from $\Xi$, it will remain in equilibrium forever unless it is disturbed and all its properties such as its temperature, pressure, energy, etc. are well defined and time invariant. Let us now disturb $\Sigma$ at time $t = 0$ by bringing it in an athermal contact (no heat exchange) with some working medium $\Sigma'$ at pressure $P' \neq P_0$, etc. We can also disturb $\Sigma$ at time $t = 0$ by bringing it in a thermal contact (resulting in heat exchange but no work exchange) with some thermalm medium $\Sigma''$ at temperature $T'' \neq T_0$. As $\Sigma$ tries to come to equilibrium, we can ask: what are $\Sigma$’s temperature $T(t)$, pressure $P(t)$, etc., examples of its instantaneous fields, if they can be defined during these nonequilibrium processes? To be consistent with the second law, we need to ensure that the definition of instantaneous pressure and temperature must result in irreversible work that is always nonnegative, and that heat always flows from hot to cold. To the best of our knowledge, this question has not been answered satisfactorily [1,2] for an arbitrary nonioequilibrium state. The question is not purely academic as it arises in various contexts of current interest in applying nonequilibrium thermodynamics to various fields such as the Szilard engine [9,11], stochastic thermodynamics [12], Maxwell’s demon [13,14], thermogalvanic cells, corrosion, chemical reactions, biological systems [15–17], etc. to name a few.

BACKGROUND Recently, we have proposed [18–22] a definition of the nonequilibrium temperature, pressure, etc. for a nonequilibrium system that is in internal equilibrium; the latter requires introducing internal variables $\xi$ as additional state variables that become superfluous in the equilibrium state. Here, we extend the definition of these fields for $\Sigma$ in any arbitrary state and verify its consistency with the second law by providing an alternative but physically more intuitive approach. The entropy $S$ in an arbitrary state may have a memory of the initial state so that it is not a state function. Such a memory is encoded in the probabilities $\{p_k(t)\}$, $k$ denoting $\Sigma$’s microstates, and is absent for a system in equilibrium or in internal equilibrium for which $S$ is a state function. In terms of $\{p_k(t)\}$ and energies $\{E_k(t)\}$, the entropy and energy are given as $S(t) = -\sum_k p_k(t) \ln p_k(t)$ and $E(t) = \sum_k E_k(t) p_k(t)$, respectively, even if $S$ is not a state function [23,24]. We can identify the two contributions in the first law $dE(t) = Q(t) - dW(t)$ [22,24] for any arbitrary infinitesimal process as

$$dW = -\sum_k p_k(t) dE_k(t), \quad dQ = \sum_k E_k(t) dp_k(t).$$

The microstate representation ensures that both $dW$ and $dQ$ are defined for any arbitrary process in terms of changes $\{dE_k\}$ and $\{dp_k\}$; in addition, they depend only on the quantities pertaining to the system [10,22,24] and not those of the medium. This makes dealing with system’s properties extremely convenient. As $dW(t)$ contains fixed $p_0 s$ so that $S$ remains fixed, it represents an isentropic quantity to be identified as work [22]. As $dQ(t)$ contains the changes $dp_0 s$, which also determine the entropy change $dS(t) = -\sum_k dp_k(t) \ln p_k(t)$, the two quantities must be related. In the following, we only consider a macroscopic system. Assuming both quantities to be extensive, this relationship must be always linear, resulting in the Clausius equality [19,20,21,22]:

$$dQ(t) = T(t) dS(t),$$

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with the intensive field $T(t)$ identified as the statistical definition of the temperature of $\Sigma$ so that heat flows from hot to cold as shown below. We only consider positive temperatures here. It may have a complicated dependence on state variables and memory through the dependence of $\{p_k(t)\}$ on the history. The work as a statistical average of $-dE_k$ remains true in general for all kinds of work including those due to $\xi$. If $dE_k$ is only due to volume change $dV$, then $dW(t) = P(t)dV$, which is also linear in $dV(t)$ as assumed above; here $P(t) \equiv -\sum p_k P_k$ is the average pressure on the walls (during any arbitrary process) with a similar complicated dependence through $\{p_k(t)\}$, and $P_k \equiv -\partial E_k/\partial V$ is the outward pressure, independent of the process, that is exerted by the $k$th microstate $\Sigma$. It immediately follows in this case that $dQ(t) \equiv dE(t)|_V$ so that the statistical temperature is also the thermodynamic temperature $\partial E/\partial S$. It can be shown that in general, $T(t)$ and $\partial E/\partial S$ are the same for a system in internal equilibrium $\Sigma$ so that the $t$-dependence in $T(t)$ is due to the $t$-dependence of the state variables. This makes $T(t)$ a state function. It is no longer a state function for a state with memory. Same comments apply to $P(t)$ or other fields.

It should be clear that $\Sigma$’s internal pressure $P(t)$, etc. have no relationship with the external pressure $P^e_0$, etc. (except in equilibrium). Thus, $dW(t)$ is in general not the negative of the work done $dW(t) \equiv -dW(t)$ by $\Sigma$ on $\Sigma$. The net work $dW(t) = dE(t) + dW(t) = dW(t) = -dW(t) \geq 0$ is irreversibly dissipated in the form of heat $d_t Q(t)$ generated within the system; see below. It follows then that $dQ(t)$ cannot represent the exchange heat $d_t Q(t) = T_d e_s(t) \leq T_d S(t)$ (Clausius inequality) between $\Sigma$ and $\Sigma$. To fully appreciate this point, we recognize that the change $dp_k(t)$ can be defined as $d_p p_k(t)$ by the interaction of the system with the medium and $d_p p_k$ by the irreversible processes going on inside the system. Accordingly, $dQ = d_c Q + d Q$ with $d_c Q = \sum E_k d p_k$ and $d Q = \sum E_k d p_k \geq 0$, and $dS = d_c S + d S$ with $d_c S = -\sum \ln p_k d p_k$ and $d S = -\sum \ln p_k d p_k \geq 0$ as a sum over microstates. One can easily check that the microstate representations of these thermodynamic quantities satisfy the thermodynamic identity $\sum$.

$$d_t Q = (T - T_0)d_e S + T d_i S.$$  

The energy conservation in the first law can be applied to the exchange process with the medium and the internal process within the system, separately as follows: $d_t E = d_e Q - d_c W$ and $d_t E = d_i Q - d_i W$. As it is not possible to change the energy of $\Sigma$ by internal processes, we conclude that $d_t E \equiv 0$ so that $d_t Q \equiv d_i W$ as noted above. This result will guide us here for the simple model calculation for an isolated system (no medium) for which $d_e p_k \equiv 0$ so that $d_p p_k = d_p q_k$.

To demonstrate that the above definition of temperature, pressure, etc. is consistent with the second law, we rewrite (4) to express $d_t S$ as a sum of two independent contributions

$$d_t S = (1/T - 1/T_0)d_c Q + d_i Q/T.$$  

Both contributions must be nonnegative in accordance with the second law. Thus, exchange heat $d_t Q$ always flows from hot to cold, and $d_i W = d_i Q \geq 0$. When $d_i W$ consists of independent contributions, each contribution must be nonnegative in accordance with the second law. This proves our assertion.

MODEL. We consider a gas of $N$ noninteracting identical structureless spin-free nonrelativistic particles, each of mass $m$, confined to a 1-dimensional box with impenetrable walls and partitions, the latter dividing the box into different sizes. The box is isolated so that $d_e Q = 0$. Initially, the gas is in thermodynamic equilibrium at temperature $T_1$ and pressure $P_1$ in state $A_1 = \Sigma$, and is confined to a predetermined (such as the leftmost) small part of the box of length $L_1$ by the leftmost partition. At time $t = 0$, the partition is instantaneously removed and the gas freely expands to a box of size $L = \alpha L_1$, $\alpha > 1$, imposed by the next partition in a nonequilibrium fashion $\Sigma$. We wish to identify the instantaneous temperature and pressure of the gas as a function of the box size $L$.

Due to the lack of inter-particle interactions, we can focus on a single particle, an extensively studied model in the literature with a very different emphasis $\Sigma$. Here, we study it from the current perspective. The particle only has non-degenerate eigenstates (standing waves) whose energies are determined by $L$ and a quantum number $k$: $p_k$ denotes its probabilities. We use the energy scale $\epsilon_0 = \pi^2 \hbar^2 / 2m L^2$ to measure the energy of the eigenstate so that $\epsilon_k(L) = k^2/\alpha^2$; the corresponding eigenfunctions are given by

$$\psi_k(x) = \langle x|k \rangle = \sqrt{2/\alpha}\sin(k\pi x/L), \ k = 1, 2, \ldots.$$  

The pressure in the $k$th eigenstate is given by $P_k(L) \equiv -\partial \epsilon_k/\partial L = 2\epsilon_k(L)/L$. The average energy and en-

![FIG. 1: Equilibrium energy $\epsilon_{eq}(T)$ (upper pair of curves) and entropy $s_{eq}(T)$ (lower pair of curves) for two different box sizes $L = 1.0$ and $1.1$ obtained by using $p_{k, eq}(\beta; L)$. The point A on $L = 1$ corresponds to $T = 4.0$ for which the energy is $\epsilon_{eq} \approx 2.7859$. The point B on $L = 1.1$ has the same energy but has a higher temperature $T \approx 4.1728$.](image)
entropy per particle, and the pressure are given by (we suppress the \( \{p_k\} \)-dependence \textit{encoding} all possible nonequilibrium states)

\begin{align}
\varepsilon(L) &\equiv \sum_k p_k \varepsilon_k, \quad s(L) = -\sum_k p_k \ln p_k \quad (6a) \\
P(L) &\equiv \sum_k p_k P_k = 2\varepsilon(L)/L. \quad (6b)
\end{align}

The \textit{equilibrium} state \( \Lambda_{eq}(T,L) \) at \textit{dimensionless} temperature \( T \) (in the units of \( \varepsilon_0 \)) is given by the Boltzmann law (\( \beta = 1/T \)) for \( p_k \):

\[ p_{k,eq}(\beta, L) = \exp(-\beta \varepsilon_k(L))/Z_0(\beta, L); \]

\[ Z_0(\beta, L) \equiv \sum \exp(-\beta \varepsilon_k(L)) \]  

The equilibrium macrostate is uniquely specified by \( \{p_{k,eq}(\beta, L)\} \).

\textbf{Results} We plot \( \varepsilon_{eq}(T, L) \) and \( s_{eq}(T, L) \) in Fig. 1 as a function of \( T \) for two different values of \( L \); \( P_{eq} = 2\varepsilon_{eq}/L \). We observe that \( \varepsilon \) decreases as \( L \) increases. To study expansion in the isolated gas, for which \( \varepsilon \) does not change, we draw a horizontal line \( \varepsilon = \varepsilon \) which crosses the \( L = 1 \) curve at \( T_{1eq} \), and the \( L = 1.1 \) curve at \( T_{2eq} \). For \( \varepsilon \approx 2.7859 \) (see below), \( T_{1eq} = 4.0 \), and \( T_{2eq} \approx 4.1728 \). As the gas expands \textit{isoenergetically} from \( L_1 = 1.0 \) to \( L = 1.1 \), its temperature varies from \( T_{1eq} \) to \( T_{2eq} \) after the equilibration time \( \tau_{eq} \). However, we learn something more from the figure. If we consider the temperature of the gas at some intermediate time \( t \) during this period, such as immediately after the \textit{free expansion} of its temperature \( T(t) \) will continuously change towards \( T_{2eq} \) in time. The equilibrium entropy also increases with \( L \) in an isothermal expansion, as expected; see the vertical line through \( A \) at \( T = 4.0 \).

To identify \( T(t) \), we proceed in three steps. In the first step, we investigate the influence of \textit{quantum expansion} on the entropy \( s \). The gas is initially in a box of length \( L_1 \) with probabilities \( p_k \) of eigenstates \( |k\rangle \equiv |k, L_1 \rangle \) and with energy and entropy per particle \( \varepsilon_i \) and \( s_i \), respectively. For an arbitrary state not in equilibrium or internal equilibrium, \( p_k \) are independent of the energies \( \varepsilon_k \) of the \( k \)th microstate. We find useful to deal with real probability “amplitude” \( a_k \) determining \( p_k \equiv |a_k|^2 \) in the following. The gas directly expands freely to a box of size \( L_1 \) or \( L_2 \), in each case starting from \( L_1 \), and we calculate the entropies of various eigenstates \( |k_1\rangle \equiv |k, L_1 \rangle \) and \( |k_2\rangle \equiv |k, L_2 \rangle \) in the two boxes:

\[ a_{k_1}^{(i)} = \sum_k a_k \langle k_1 | k \rangle, \quad a_{k_2}^{(i)} = \sum_k a_k \langle k_2 | k \rangle, \]

from which we calculate the entropies \( s_1^{(i)} \) and \( s_2^{(i)} \), respectively; the superscript is a \textit{reminder of the memory effect} since these quantities depend on the initial state through \( p_k \). The coefficients \( \langle k_1 | k \rangle \), etc. are \textit{calculated}.

\[ \langle k_1 | k \rangle = \frac{2k \sin^2(-\frac{k}{2})}{\pi(k^2-a^2k_2^2)} \sin(\frac{k_1 \pi}{\alpha}). \]

Because of the ”deterministic” laws of quantum mechanics and the completeness of the eigenstates, the amplitude \( \sum_k a_k^{(i)} |k_2 \rangle \langle k_1 \rangle \) of the eigenstate \( |k_2\rangle \) after expansion from \( L_1 \) to \( L_2 \) is exactly \( a_{k_2}^{(ii)} \). Thus, the entropy \( s_2^{(ii)} \) obtained from the direct expansion \( L_0 \rightarrow L_2 \).
is the same as the entropy obtained from the expansion sequence \( L_1 \rightarrow L_2 \). We have also checked that the two entropies are the same to within our numerical accuracy in our computation. This means that the final \( (L_f) \) entropy has a memory of the initial \( (L_i) \) state, but not of the paths from \( L_i \) to \( L_f \). Thus, the entropy \( s(0)(\varepsilon, L) \) in pure quantum mechanical evolution from a given initial state is not a state function of \( \varepsilon \) and \( L \). This is an important observation.

The memory effect results in a nonequilibrium state. The consequences of the latter can also be appreciated by considering the eigenstate probabilities \( p_k \) for different \( k \) which is shown in the main frame in Fig. 2 for \( L = 1.1 \). It appears to fall off very rapidly, just as \( p_{k,eq} \). However while \( p_{k,eq} \) monotonically decreases with \( k \), \( p_k \) has an oscillatory behavior, as shown in the inset (a) for \( k \) between 25 and 50, where we compare the two probabilities; here the former is effectively zero. The fine structure of this oscillatory behavior becomes obvious by considering the behavior of \( \ln(p_1/p_k) \), which is plotted in the inset (b), for \( k \geq 1 \). The oscillations are in conformity with the presence of sine in \( \langle k_1 | k_0 \rangle \), and should not be a surprise.

In the second step, we determine \( T \) and \( P \) for the nonequilibrium state \( A(\varepsilon_1, L) \) in a box of size \( L \) after free expansion from \( L_i \). The initial state \( A_1 \) is an equilibrium state \( A_{k,eq}(T = 4.0 \ (\varepsilon_1 \approx 2.7859), L_i = 1.0) \) for which \( s_{i,eq} \approx 0.94 \). The entropy difference \( \Delta s \equiv s(L = 1.1) - s_{i,eq} \approx 0.96 - 0.94 = 0.12 \) is positive, which is expected in a free expansion. For the determination of the temperature, we proceed as follows. We allow the gas to freely expand \( (P'_0 = 0) \) from \( L \) by a "differential" amount \( dL \approx 0.0000001 \) to \( L' \). In this differential expansion, \( dQ = d_i Q = d_i W (d_i Q = 0) \), and \( d_i W = P(L) dL \). We also compute the change in the entropy \( ds \equiv s(L') - s(L) \). The ratio \( PdL/ds \), see Eq. (2), determines the temperature \( T \) of the nonequilibrium gas. For \( L = 1.1 \), we determine the temperature to be \( T(1.1) \approx 4.365 \) using this differential method, which lies outside the equilibrium temperatures \( T_{eq}(1.0) = 4.0 \), and \( T_{eq}(1.1) = 4.173 \) quoted above. As we will show below, the higher nonequilibrium temperature is due to "wider" microstate distribution relative to that for the equilibrium state. The results for \( T(L) \) for different \( L \) in the free expansion \( A_{i,eq} \rightarrow A(\varepsilon_1, L) \) are shown in Fig. 3.

To add to the creditability of the above differential method for \( T \), we apply it to determine \( T \) for the equilibrium state \( A_{i,eq}(T = 4.0, L = 1.0) \). For such a state, the ratio \( r = \ln(p_1/p_k)L^2/(k^2 - 1) \) is \( r = 1/T \) for all \( k \); see Eq. (4). As \( p_{k,eq} \) falls exponentially with \( k^2 \), we truncate the number of microstates to \( k \leq k_{tr} \) for which \( p_{k,eq} \geq 10^{-15} \). This limits the number of microstates to \( k \leq k_{tr} = 13 \). If we truncate using \( p_{k,eq} \geq 10^{-22} \), then we need to consider \( k \leq k_{tr} = 15 \). Thus, truncating the number of microstates to \( k_{tr} \) is computationally reasonable. The above calculation for the temperature with \( k \leq k_{tr} = 13 \) gives \( T = 4.000000 \) to the first five decimal places, which adds to its creditability.

We now ask the following question: What will happen if we consider only the first \( \kappa \) microstates to determine the temperature, etc. by setting \( p_{k,eq} = 0 \) for \( k > \kappa \). Such truncated states are obviously not equilibrium states. To ensure that the probabilities add up to 1, we normalize the probabilities, which does not affect the ratio \( r \), as follows: \( p_{k,eq} = p_{k,eq}/\sum p_{k,eq} \). The results for the temperature, energy and entropy are shown in Fig. 4. In contrast, \( r \) does not depend on the value of \( \kappa \) as shown in the inset for \( \kappa \leq 7 \). But what we observe is an interesting phenomenon. As the number \( \kappa \) increases, that is as the distribution gets "wider," the temperature gets higher and eventually gets to its limiting value of 4.0.

The pressure is determined by Eq. (6b) by setting \( p_{k,eq} = 0 \) for \( k > \kappa \). This is the statistical method (method 1) to compute \( P(L) \). Accordingly, \( P(L) \) in an isoenergetic process is a decreasing function of \( L \). The ratio \( P(L)/\varepsilon_1 \) is independent of the \( T_i \) of the initial state, which is confirmed by our computation as shown by the upper curves for the two choices \( T_i = 1.0 \) and \( T_i = 4.0 \) in Fig. 3. There is another way (method 2) to determine the pressure in terms of the temperature, which is based on a thermodynamic relation: \( P/T = (\partial s/\partial L)_T \). We use the ratio of the "differentials" \( ds \) and \( dL \) to determine \( P/T \). We now use the statistical temperature in Fig. 3 in this ratio to compute the thermodynamic pressure \( P \). The results are found to be indistinguishable from those shown in Fig. 3 by method 1, thus justifying our claim that the determination of our nonequilibrium temperature is meaningful as the "internal" temperature of the system in that the two different methods to determine the pressure give almost identical values within our nu-
merical accuracy.

As the memory of the initial state in $s_1^{(i)}, s_2^{(i)}$, etc. cannot disappear by deterministic quantum evolution, some other mechanism is required for equilibration to come about in which the nonequilibrium entropy will gradually increase until it becomes equal to its equilibrium value. One possible mechanism based on the idea of “chemical reaction” among microstates has been proposed earlier [23]. We will consider the consequences of this approach elsewhere.

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[29] Following modern notation [27, 28], exchange of any extensive quantity $Y(t)$ with the medium and its change within the system carry the inner suffix e and i, respectively: $dY(t) \equiv d_Y(t) + d_i Y(t)$. For example, we write $dS(t) = d_e S(t) + d_i S(t)$ as the two components of the entropy change $dS(t)$ in a body: $dS(t) \equiv d_e S(t) + d_i S(t)$. A similar partition $d_{p_e}(t) = d_{p_e}(t) + d_{p_i}(t)$ can also be made.
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