Thermodynamic definition of mean temperature

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The notion of mean temperature is crucial for a number of fields including climate science, fluid dynamics and biophysics. However, so far its correct thermodynamic foundation is lacking or even believed to be impossible. A physically correct definition should not be based on mathematical notions of the means (e.g. the mean geometric or mean arithmetic), because they ignore the peculiarities of the notion of temperature, and because they are not unique. We offer a thermodynamic definition of the mean temperature that is based upon the following two assumptions. First, as the correct definition should necessarily involve equilibration processes in the initially non-equilibrium system, the mean temperature is bounded from below and above via looking at (respectively) the reversible versus fully irreversible extremes of equilibration. Second, within the thermodynamic approach we assume that the mean temperature is determined mostly by energy and entropy. Together with the dimensional analysis, the two assumptions lead to a unique definition of the mean temperature. The mean temperature for ideal and (van der Waals) non-ideal gases with temperature-independent heat capacity is given by a general and compact formula that (besides the initial temperatures) only depends on the heat-capacities and concentration of gases.

Many non-equilibrium situations are described by mean temperature in a quasi-equilibrium manner. Climate is defined with respect to a mean temperature, while climate change discussions are largely based on global mean temperatures of Earth’s surface \[1–6\]. Mean temperature and deviations from it are widely used in various fields, e.g. length, volume, and (to some extent) energy. Here defining the mean amounts to taking the two systems with different (say) volumes together, calculating the total volume and dividing over the number of systems. But temperature is not an additive quantity.

(iii) Temperature is defined with respect to a conventionally chosen thermometer \[13,14\]. The readings \(t_1\) and \(t_2\) of two thermometers 1 and 2 relates to each other via a monotonous transformation \(t_1 = f(t_2)\) \[13,14\]. Hence the notions of larger and smaller are well-defined for temperature, but mathematical means are not covariant with respect to \(f(x)\), in contrast to physical quantities (energy, entropy, pressure \textit{etc} that are invariant. One particular example of \(f(x)\) is an affine transformation \(f(x) = ax + b\), where \(a\) and \(b\) are constants. Three basic scales—Celsius, Fahrenheit, and Kelvin—relate to each other via affine transformations. The arithmetic mean (but not other means) is covariant with respect to an affine transformations, but is not covariant with respect to more general monotonous transformations; e.g. to \(f(x) = 1/x\). Indeed, frequently the inverse temperature \(\beta = 1/T\) provides a better physical description than \(T\) itself, e.g. because it provides a better of account non-equilibrium physics \[13\]. Spin physics employs \(\beta\) instead of \(T\), also because in that field \(\beta\) passing through zero is usual, unlike “dramatic” changes implied by \(T = 1/\beta\) passing through the infinity \[17\]. Also, the usage of \(\beta\) (instead of \(T\)) makes the third law intuitive, since this law now tells about impossibility to reach \(\beta = \infty\) \[13\].

(iv) Temperature is defined only in equilibrium \[13\]. This means that for defining a mean temperature in a non-equilibrium state we should invoke physically meaningful equilibration processes. But they are not unique.

We propose a thermodynamic definition of the mean temperature that solves the above issues. We start by setting upper and lower bounds to the mean temperature. These bounds describe two extremes of equilibration processes: one that is reversible and thermally-isolated, releasing work, and one that is completely irreversible and energy-isolated, increasing entropy by dissipating the available work. We postulate that respective temperatures \(T\) and \(\bar{T}\) \((\bar{T} < T)\) are lower and upper bounds of the mean temperature \(\bar{T}\). Next, we assume that within the thermodynamic description, the mean temperature \(\bar{T}\) is defined only via entropies and energies of the initial (non-equilibrium) state and possible final equilibrium state. This assumption, along with a dimen-
sional analysis, suffices to define the mean temperature \( \bar{T} \). It holds \( T \leq \bar{T} \leq \tilde{T} \), and depends both on the initial non-equilibrium state of the considered system and also on the very substance it refers to; e.g. the mean temperature for two pieces of iron having temperatures \( T_1 \) and \( T_2 \) will be different from two pieces of wood having the same temperatures \( T_1 \) and \( T_2 \). However, for a class of systems relevant for atmospheric physics—ideal and van der Waals non-ideal gases with a temperature-independent heat-capacity (cf. §1 of [33])—\( \bar{T} \) holds a general expression that (aside of the initial temperatures) depends only on heat-capacities and concentrations of gases.

Consider two equilibrium systems \( A_1 \) and \( A_2 \) at different absolute temperature \( T_1 \) and \( T_2 \), with the number of particles \( N_1 \) and \( N_2 \), volumes \( V_1 \) and \( V_2 \), internal energies \( U_1(T_1, V_1, N_1) \) and \( U_2(T_2, V_2, N_2) \), and entropies \( S_1(T_1, V_1, N_1) \) and \( S_2(T_2, V_2, N_2) \), respectively. We shall work with the absolute temperature scale (in energy units, i.e. with \( k_B = 1 \)), but at several places we emphasize the covariance of our conclusions with respect to monotonous transformations of temperature.

We assume that \( A_1 + A_2 \) is a thermally isolated system. We allow \( A_1 + A_2 \) to equilibrate and reach some joint temperature, which can be then related to the mean temperature. The equilibration process is not unique, it depends on the external conditions [13]; e.g. it depends on whether and to which extent we allow for work-extraction from \( A_1 + A_2 \). Below we resolve this non-uniqueness. We consider only processes that proceed via thermal contacts; i.e. they are realized at fixed values of the volumes \( (V_1, V_2) \) and the particle numbers \( (N_1, N_2) \). The reason for this is discussed in §2 of [23]. Hence we omit the arguments \( (V_1, N_1) \) and \( (V_2, N_2) \) for energy and entropy.

**Reversible equilibration.** \( A_1 \) and \( A_2 \) couple through a working body \( B \), which sequentially interact with \( A_1 \) and \( A_2 \) via weak thermal contacts. Between interactions \( B \) delivers work to the external source [13]. The thermodynamic state of \( B \) changes cyclically. Hence the overall entropy change is given by the change of the entropies of \( A_1 \) and \( A_2 \). The process is reversible, and the overall entropy stays constant:

\[
S_1(T_1) + S_2(T_2) = S_1(\bar{T}) + S_2(\tilde{T}),
\]

where \( \bar{T} \) is the final temperature, which is the same for \( A_1 \) and \( A_2 \). Since \( A_1 + A_2 \) is thermally isolated due to [14], the overall energy deficit is the extracted work:

\[
U_1(T_1) + U_2(T_2) - U_1(\bar{T}) - U_2(\tilde{T}) \geq 0.
\]

Fig. 1 illustrates the situation of [11, 2] on the energy-entropy diagram. It is seen that possible non-equilibrium states \( (U_{in}, S_{in}) \) are bound (from left) by an increasing and concave equilibrium energy-entropy curve. The reason of concavity is reminded in the caption of Fig. 1. For our situation \( U_{in} = U_1(T_1) + U_2(T_2) \) and \( S_{in} = S_1(T_1) + S_2(T_2) \). Note from Fig. 1 that [2] is the maximal work that can be extracted under the restriction of the second law and fixed \( (V_1, N_1) \) and \( (V_2, N_2) \):

\[
U_1(\bar{T}) + U_2(\tilde{T}) = \min_{T_1, T_2} \left[ U_1(\bar{T}_1) + U_2(\tilde{T}_2) \right],
\]

where the minimization is conditioned by \( S_1(T_1) + S_2(T_2) \leq S_1(\tilde{T}_1) + S_2(\bar{T}_2) \). Indeed, if we allow more general processes, where the final entropy is larger than \( S_{in} = S_1(T_1) + S_2(T_2) \), then the final energy is also larger than \( U_1(T) + U_2(T) \) due to the fact that the equilibrium energy-entropy curve \( S(E) \) is increasing; see Fig. 1.

It is natural for relaxation to be accompanied by work-extraction. Within atmospheric thermodynamics, work-extraction means increasing the hydrodynamic kinetic energy due to internal energy and refers to the emergence of a macroscopic motion (wind, storm or circulation) in a non-equilibrium state [19, 20]; see [16, 22] for reviews. Carefully accounting for this energy balance requires fluid dynamic consideration; see e.g. [28]. Ref. [21] studied the maximal extracted work and the maximal entropy increase as features of a non-equilibrium atmosphere; see [22] for a review.

**Fully irreversible equilibration.** The second pertinent scenario of equilibration looks at another extreme. Now \( A_1 \) and \( A_2 \) are isolated from the rest of the world and are subject to the fully irreversible equilibration via thermal contacts; i.e. again \( (V_1, N_1) \) for \( A_1 \) and \( (V_2, N_2) \) for \( A_2 \) stay fixed. Now the total energy is conserved

\[
U_1(T_1) + U_2(T_2) = U_1(\bar{T}) + U_2(\tilde{T}),
\]

defining the final temperature \( \bar{T} \). The entropy increase is clearly positive:

\[
S_1(\bar{T}) + S_2(\tilde{T}) - S_1(T_1) - S_2(T_2) > 0.
\]

As seen from Fig. 1, (5) is the maximal entropy increase for the conserving energy plus fixed \( (V_1, N_1) \) and \( (V_2, N_2) \):

\[
S_1(\bar{T}) + S_2(\tilde{T}) = \max_{T_1, T_2} \left[ S_1(\bar{T}_1) + S_2(\tilde{T}_2) \right],
\]

where the maximization is conditioned by \( U_1(T_1) + U_2(T_2) = U_1(\bar{T}_1) + U_2(\tilde{T}_2) \).

**Upper and lower bounds for the mean temperature.** As we confirm below, the temperatures \( \bar{T} \) and \( \tilde{T} \) hold

\[
\min[T_1, T_2] \leq \bar{T} \leq \tilde{T} \leq \max[T_1, T_2],
\]

which naturally implies that all other temperatures found via partially irreversible processes will be located between \( \bar{T} \) and \( \tilde{T} \); see Fig. 1.

Our first assumption reads: the mean temperature \( \bar{T} \) should locate between \( \bar{T} \) and \( \tilde{T} \):

\[
\bar{T} \leq \tilde{T} \leq \tilde{T}
\]

The motivation for [9] is that once the temperature relates to the heat content, we should decide what to do
with the available work. Two extreme options are to dissipate it completely (̂T), or to extract it fully (T). We cannot add any external work, since this will potentially change the heat content. Moreover, if we start adding work to the overall system A1 + A2, the final temperature can be made arbitrary large.

We emphasize that ̂T and T are covariant with respect to monotonous transformations of the absolute temperature. This follows from the very definitions \( \alpha \). Put differently, ̂T and T are covariant with respect to employing any other reasonable thermometer instead of the thermometer that leads to the absolute temperature.

Mean temperature. Guided by \( \alpha \), we postulate that the mean temperature ̂T is found through a four-variable function of the initial and final energy and entropy:

\[
\hat{T} = \arg\max_F \{ U_1(T) + U_2(T) + S_1(T) + S_2(T), \ S_1(T_1) + S_2(T_2) - U_1(T_1) - U_2(T_2)\}. \tag{9}
\]

̂T in (9) should be invariant with respect to changing dimensions of the entropy and energy, as well as adding to these quantities arbitrary constants b and d \( \alpha \):

\[
S \to aS + b, \quad U \to cU + d, \quad a > 0, \quad c > 0, \tag{10}
\]

where the constants a and c come from changing the dimensions. In addition, \( \alpha \) should hold \( \alpha \). Indeed, the invariance with respect to changing the dimensions is a natural condition to demand, while the invariance with respect adding arbitrary constants reflect the freedom energy and entropy enjoy in thermodynamics.

The only expression that holds all above conditions, and is invariant with respect to \( \alpha \), reads \( \alpha \):

\[
\hat{T}(\alpha_1, \alpha_2) = \arg\max_T \{ [U_1(T_1) + U_2(T_2) - U_1(T) - U_2(T)]^{\alpha_1} [S_1(T) + S_2(T) - S_1(T_1) - S_2(T_2)]^{\alpha_2} \}. \tag{11}
\]

where \( \alpha_1 \geq 0 \) and \( \alpha_2 \geq 0 \) are weights. All other possibilities are equivalent to (11) in one way or another.

Note that for \( \alpha_1 \to 0 \) and \( \alpha_2 \to 0 \) we revert to (resp.) \( \alpha \) and \( \alpha \). It should be also clear that \( \hat{T} \leq \overline{T}(\alpha_1, \alpha_2) \leq \bar{T} \). How to choose \( \alpha_1 \) and \( \alpha_2 \)? First note that instead of the function to be maximized in (11) we can maximize its logarithm, which makes clear that only the ratio \( \alpha_1/\alpha_2 \) is important for \( \overline{T}(\alpha_1, \alpha_2) \). In other words, we can assume \( \alpha_1 + \alpha_2 = 1 \). Once we do not know these weights, the ignorance (or the most unbiased, or the maximum entropy) interpretation forces us to choose \( \alpha_1 = \alpha_2 = 1/2 \). Thus we end up from (11) to the final definition of the mean temperature:

\[
\hat{T} = \overline{T}(1/2, 1/2). \tag{12}
\]

Eq. (12) achieves a balance between no work extraction (complete irreversibility) and the complete reversibility: now some work is still extracted, but the entropy does increase. The unique argmax of (12) automatically appears in the interval [̂T,̂T]. In contrast to a naive definition (̂T + ̂T)/2, ̂T in (12) is invariant with respect to monotonic changes of temperature (i.e., going from one
reasonable thermometer to another), since it is defined via optimization of thermodynamic variables.

To extend the physical meaning of (12) note that $\bar{T}$ from (12) is the temperature that corresponds to values $(\bar{U}, \bar{S})$ found via

$$\bar{(U,S)} = \arg\max_{S,U} \left[(S - S_{in})(U_{in} - U)\right],$$

(13)

where the maximization is carried out over all allowed physical (also non-equilibrium) values of $S$ and $U$. For consistency with (12) we have $S_{in} = S_{i}(T_1) + S_{2}(T_2)$, and $U_{in} = U_{i}(T_1) + U_{2}(T_2)$, but (13) applies to any non-equilibrium initial state $(S_{in}, U_{in})$; e.g. several initially non-interacting, equilibrium systems at different temperatures, or non-equilibrium systems with effective temperatures, or non-equilibrium systems with effective temperatures [32]. To understand (13), recall from Fig. 1 that those physical values of energy and entropy are bound into a convex domain by the equilibrium curve $S(U)$. The maximization in (13) is reached in that curve; otherwise one can always increase $S$ or decrease $U$ so as to reach this curve. We also naturally have $\bar{S} \leq S \leq \bar{S}$ and $\bar{U} \leq \bar{U} \leq \bar{U}$; see (13) and Fig. 1. The maximum in (13) [i.e. also in (12)] is unique; see §3 of [32]. Eq. (13) can be applied without demanding that $(\bar{U}, \bar{S})$ are in equilibrium, and without requiring the bounds [8]. These features come out automatically from (13), which can be generalized to cases where there are additional (dynamic) restrictions towards attaining the equilibrium curve.

Ideal gases. The simplest case is that of $M$ ideal gases with volumes $V_k$, number of particles $N_k$, internal energies $U_k$, entropies $S_k$, constant (i.e. temperature-independent) fixed-volume heat-capacities $c_k$, and temperatures $T_k$ (k = 1, ..., M):

$$S_k = N_k \ln \frac{V_k}{N_k} + N_k c_k \ln T_k, \quad U_k = N_k c_k T_k,$$

(14)

where in $S_k$ and in $U_k$ we omitted certain inessential constants. Now $\bar{T}$ and $\bar{T}$ read from (3) [11]:

$$\bar{T} = \prod_{i=1}^{M} \frac{T_{ni c_i}}{N_i}, \quad \bar{T} = \sum_{i=1}^{M} \frac{n_i c_i}{N} T_i,$$

(15)

where $\bar{c}$ is the mean heat-capacity and $n_i$ are concentrations. Hence $\bar{T} (\bar{T})$ in (15) reduces to a weighted geometric (arithmetic) average with weights $n_i c_k / \bar{c}$. The arithmetic and geometric means in (15) for ideal gases have temperature-independent heat-capacities, i.e. they do not hold generally.

Now (12) is represented as $\max_{T} \left[(T - T) \ln(T/\bar{T})\right]$. The maximization is carried out by differentiating:

$$\bar{T} = \bar{T} / W \left[\ln \bar{T}/\bar{T}\right],$$

(17)

where $W[z]$ is the Lambert special function that solves the equation $We^W = z$. It has various applications in physics [32], and is tabulated with major computational platforms; e.g. Python and Mathematica (as PolyLog[z]). In the simplest case of equal heat-capacities, $c_1 = ... = c_M$, we find from (17) for $M = 2$ (with obvious generalization to $M > 2$):

$$\bar{T} = \frac{T_1 + T_2}{2W \left[\ln (T_1 + T_2)/(2\sqrt{T_1 T_2})\right]}.$$
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Supplementary Material for
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This Supplementary Material consists of 3 chapters. §1 reminds thermodynamics of van der Waals non-ideal gas and shows that the formulas for the mean temperature hold also for this gas. §2 explain why we restricted thermalization processes in the main text. §3 discusses a technical issue related to the uniqueness in optimization. Formulas continue the numbering of the main text.

§1. van der Waals non-ideal gas

For the van der Waals non-ideal gas model entropy and energy read, respectively \[ \text{[1]} \] [cf. (14)]:

\[
S_k = c_k N_k \ln T_k + N_k \ln \left( \frac{V_k - N_k b_k}{N_k} \right),
\]

(19)

\[
U_k = c_k N_k T_k - \frac{N_k^2 a_k}{V_k}, \quad k = 1, \ldots, M,
\]

(20)

where \(c_k\) is the constant-volume heat capacity—which are again assumed to be constants—while \(a_k\) and \(b_k\) are van der Waals parameters. Recall that \(a_k > 0\) enters only into the energy, i.e. it characterizes the inter-particle interaction, while \(b_k > 0\) enters only the entropy, as it stands for the excluded volume. It should be clear from (19) that \(\frac{N_k b_k}{V_k}\) holds \(0 < 1 - \frac{N_k b_k}{V_k}\). An upper bound on \(1 - \frac{N_k b_k}{V_k}\) comes from the thermodynamic stability condition \(\frac{\partial H}{\partial V}/T < 0\) [1]. Hence two bounds together can be written as:

\[
0 < 1 - \frac{N_k b_k}{V_k} < \sqrt{\frac{T_k}{2a_k \frac{N_k}{V_k}}},
\]

(21)

Given these restrictions on the van der Waals parameters we find back from \(\text{[12]} \text{[11]} \text{[15]} \text{[18]}\) the same formulas \(\text{[15]} \text{[18]}\). In particular, they apply for defining averages between metastable states described by the van der Waals equation.

§2. Why we do not consider more general equilibration processes?

In the main text we restricted ourselves with reversible and fully irreversible processes that proceed via thermal contacts; i.e. they are realized at fixed values of the volumes \((V_1, V_2)\) and the particle numbers \((N_1, N_2)\). In particular, we did not involve pressure differences into the work-extraction, because even when the equilibrium systems \(A_1\) and \(A_2\) have initially the same temperature \(T\), their final temperature (after work has been extracted from pressure differences as well) will be lower than \(T\), as we show below. This would obviously contradict our intention of defining the mean temperature, since e.g. condition \(\text{[1]}\) will not anymore hold. Similar issues arise when \(A_1\) and \(A_2\) are composed of different (distinguishable) particles, and we allow the mixing of gases during the work-extraction. Then the final temperature will be lower than \(T\) due to the Gibbs term even when initial pressures and temperatures are equal; see §2.1 below.

This issue is not restricted to the reversible mode of operation only. For example, during an irreversible mixing of two non-ideal gases \(A_1\) and \(A_2\) having initially the same temperature \(T\), their final temperature will be lower than \(T\), if the irreversible process is extended to include pressure differences; see §2.1.

Thus, the definition of a mean temperature in a non-equilibrium system requires equilibration processes that proceed mostly thorough thermal conductivity. §2.1 and §2.2 show that there are reversible and irreversible processes that are not restricted to thermal contacts and that are not suitable for determining the mean temperature for a number of interesting reasons.

§2.1 Ideal gases

Recall (14) for entropy and energy of \(k = 2\) ideal gases at (initial) temperatures \(T_k\). The two gases together form a thermally isolated system. The total volume \(V_1 + V_2\) and the total number of particles \(N_1 + N_2\) are conserved.

First we assume that \(c_1 \neq c_2\), i.e. the gases are different. Let now they mix together and equilibrate via an entropy conserving process. Hence only \(V_1 + V_2\) and \(N_1 + N_2\) are conserved, but not \(V_1\) and \(N_1\) separately. In the final equilibrated state each gas occupies volume \(V = V_1 + V_2\) and they both have the same temperature \(\hat{T}\). Hence the condition that the final entropy equals initial entropy reads from (14)

\[
\sum_{k=1}^{2} N_k \left( \ln \frac{V}{N_k} + c_k \ln \hat{T} \right) = \sum_{k=1}^{2} N_k \left( \ln \frac{V_k}{N_k} + c_k \ln T_k \right).
\]

(22)

Now (22) leads to

\[
\hat{T} = e^{\frac{1}{2} \sum_{i=1}^{2} n_i \ln \frac{1}{v_i} \prod_{l=1}^{2} T_{l \text{ide}} / \tilde{c}},
\]

(23)

\[
n_k = \frac{N_k}{\sum_{i=1}^{2} N_i}, \quad v_k = \frac{V_k}{\sum_{i=1}^{2} V_i}, \quad \tilde{c} = \frac{\sum_{i=1}^{2} n_i c_i}{n_1 c_1 + n_2 c_2},
\]

(24)

where \(\sum_{i=1}^{2} n_i \ln \frac{1}{v_i} \geq 0\) is the Gibbs mixing term. We now have for \(T_1 = T_2\):

\[
\hat{T} = e^{\frac{1}{2} \sum_{i=1}^{2} n_i \ln \frac{1}{v_i} < T_1 = T_2},
\]

(25)
i.e. this equilibration scheme is not suitable for the definition of a mean temperature.

Now assume that the gases are identical, hence \( c_1 = c_2 = c \). The final equilibrated gas should be treated as a single entity with number of particles \( N = N_1 + N_2 \), temperature \( \tilde{T}_\text{id} \) and volume \( V = V_1 + V_2 \). The constant entropy condition reads instead of (23)

\[
N \ln \frac{V}{N} + c \ln \tilde{T}_\text{id} = \sum_{k=1}^{2} N_k \left( \ln \frac{V_k}{s_k} + c \ln T_k \right), \tag{26}
\]

which implies [cf. (24)]

\[
\tilde{T}_\text{id} = e^{-\frac{1}{c} \sum_{l=1}^{2} n_l \ln \frac{\mu_l}{\mu_l}}, \tag{27}
\]

Recall from the fact that \( \sum_{l=1}^{2} n_l \ln \frac{\mu_l}{\mu_l} = 0 \) only when \( n_l = v_l \) (\( l = 1, 2 \)). It is seen again that even when \( T_1 = T_2 \) in (27) we still have that \( \tilde{T}_\text{id} < T_1 = T_2 \). Noting the equation of state \( P_k V_k = N_k T_k \) (where \( P_k \) is pressure and \( k = 1, 2 \)) for initial gases, we see that for \( T_1 = T_2 \) we can have \( \sum_{l=1}^{2} n_l \ln \frac{\mu_l}{\mu_l} > 0 \) only when \( P_1 \neq P_2 \). Hence the inequality of pressures in the initial state makes \( \tilde{T}_\text{id} < T_1 = T_2 \).

Thus, due to \( \tilde{T}_\text{id} < T_1 = T_2 \) and \( \tilde{T} < T_1 = T_2 \), processes described by (24) are not suitable for defining a lower bound on the mean temperature.

\[ \text{§2.2 Non-ideal gases} \]

The analysis of §2.1 will be repeated for non-ideal gases, since there novel points in this case.

Recall from (19) the van der Waals non-ideal gas model. For simplicity we take \( c_k = c > 0 \) (temperature-independent constant), \( a_k = a > 0 \), \( b_k = b > 0 \), and \( k = 1, 2 \). Let us assume that the two gases mix in a completely irreversible way and reach temperature \( \tilde{T} \) (or \( \tilde{T}_\text{id} \)) that is determined from the energy conservation:

\[
\tilde{T} = \sum_{k=1}^{2} n_k T_k - \frac{a N}{c V} \sum_{k=1}^{2} n_k \frac{n_k}{v_k} (1 - \frac{1}{v_k}), \tag{29}
\]

\[
\tilde{T}_\text{id} = \sum_{k=1}^{2} n_k T_k - \frac{a N}{c V} \sum_{k=1}^{2} n_k^2 (1 - \frac{1}{v_k}), \tag{30}
\]

where \( n_k \) and \( v_k \) are defined by (24). Eq. (29) refers to the distinguishable situation (non-identical gases), where in the final state we still have 2 gases with particle numbers \( N_1 \) and \( N_2 \) occupying volume \( V = V_1 + V_2 \). Eq. (30) refers to identical gases, where the final state is a single gas at volume \( V = V_1 + V_2 \), particle number \( N = N_1 + N_2 \) and temperature \( T_\text{id} \). We emphasize that for non-ideal gases also the irreversible mixing temperature starts to feel whether the particles are identical.

Note from (29) to (30) that

\[
\tilde{T} < \sum_{k=1}^{2} n_k T_k, \quad \tilde{T}_\text{id} < \sum_{k=1}^{2} n_k T_k. \tag{31}
\]

The second relation in (31) is obvious from \( v_k < 1 \). The first relation follows from (28) upon noting there \( \ln \frac{\mu}{\mu} \leq \frac{\mu}{\mu} - 1 \). Eq. (31) confirms that \( T_1 = T_2 > \tilde{T} \) and \( T_1 = T_2 > \tilde{T}_\text{id} \), i.e. this irreversible process is not suitable for defining an upper bound on the mean temperature.

\[ \text{§3. The maximum in (13) is unique.} \]

Let us show that the maximum in (13) [hence also in (12)] is unique. The mathematical structure of this argument is taken from [2]; cf. also [3]. Indeed, if the maximum is reached at two different points \((U_1, S_1)\) and \((U_2, S_2)\) such that

\[
(S_1 - S_\text{in})(U_\text{in} - U_1) = (S_2 - S_\text{in})(U_\text{in} - U_2), \tag{32}
\]

then \( \frac{1}{2}(U_1 + U_2, S_1 + S_2) \) is also in the maximization domain of (13), because that domain is a convex set. This fact follows from the concavity of \( S(U) \) curve in Fig. 1 Now

\[
\frac{1}{4}(S_1 - S_\text{in} + S_2 - S_\text{in})(U_\text{in} - U_1 + U_\text{in} - U_2) >
(S_1 - S_\text{in})(U_\text{in} - U_1) = (S_2 - S_\text{in})(U_\text{in} - U_2), \tag{33}
\]

contradicts to the assumption that \((S_1 - S_\text{in})(U_\text{in} - U_1) = (S_2 - S_\text{in})(U_\text{in} - U_2)\) provide maxima. Hence, the maximum in (13) is unique: \((U_1, S_1) = (U_2, S_2)\).

\[ \text{[1] L.D. Landau and E.M. Lifshitz, Statistical Physics, Part I (Pergamon Press, 1980).} \]
\[ \text{[2] A.E. Roth, Axiomatic Models of Bargaining (Springer Verlag, Berlin, 1979).} \]
\[ \text{[3] S. G. Babajanyan, A. E. Allahverdyan, and Kang Hao Cheong, Energy and entropy: Path from game theory to statistical mechanics, Phys. Rev. R 2, 043055 (2020).} \]