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Appendix XI. Derivation of a relation between volumes and the number of molecules in a spontaneously expanding ideal gas

Abstract

A mathematical relation between a quotient between two future-directed probabilities of a spontaneously expanding ideal gas, on the one hand, and the number of molecules in the same gas and the volumes they occupy, on the other, was recently derived from the formula for *statistical entropy difference*. In the present paper, a more straightforward derivation is presented, which does not take the entropy concept into account. First, the relation is derived for the special case of two volumes that are not overlapping and then for the case of freely expanding ideal gas. The resulting derivation can be considered as a partly verification of the aforementioned formula.

1 Introduction

In a recent article (Skoruppa, 2022b) an equation, describing *statistical entropy difference* between two macroscopically well-defined states, A and B, in an isolated evolution, is derived:

$$S_A - S_B = k_B \cdot \ln \frac{p(A[t_1 + \tau]|B[t_1])}{p(B[t_2 + \tau]|A[t_2])} \, , \tau > 0, \tag{1}$$

where k_B is Boltzmann's constant and τ is an arbitrary positive time interval. This relation shows some resemblance with the well-known formula for entropy increase of an ideal gas, expanding from one equilibrium state to another, as a function of the number of molecules (in mole), n, and the initial and final volumes of the gas:

$$S_{\mathbf{II}} - S_{\mathbf{I}} = n \cdot R \cdot \ln \frac{V_{\mathbf{II}}}{V_{\mathbf{I}}} \, , \tag{2}$$

where, R is the molar gas constant.

Let $p_N(V_{\mathbf{B}}[t + \tau]|V_{\mathbf{A}}[t])$ denote the conditional probability that N molecules, contained in volume $V_{\mathbf{A}}$ at the point in time, t, are contained

in volume $V_{\mathbf{B}}$ at later point in time, $t+\tau$. Then, as is already stated in Skoruppa (2022b, Section 7), equations (1) and (2) combine to

$$\begin{aligned} k_B \cdot \ln \frac{p_N(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p_N(V_{\mathbf{I}}[t'_0+\tau]|V_{\mathbf{II}}[t'_0])} &= n \cdot R \cdot \ln \frac{V_{\mathbf{II}}}{V_{\mathbf{I}}} \\ \Rightarrow \frac{p_N(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p_N(V_{\mathbf{I}}[t'_0+\tau]|V_{\mathbf{II}}[t'_0])} &= \left(\frac{V_{\mathbf{II}}}{V_{\mathbf{I}}}\right)^{\frac{n\cdot R}{k_B}} \\ \Rightarrow \frac{p_N(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p_N(V_{\mathbf{I}}[t'_0+\tau]|V_{\mathbf{II}}[t'_0])} &= \left(\frac{V_{\mathbf{II}}}{V_{\mathbf{I}}}\right)^{N} , \end{aligned} \tag{3}$$

where N is the number of molecules in the gas. An important condition for the above expression is that the molecules are equally distributed in the two volumes at the given points in time, i.e. that the molecule systems are in equilibrium both before and after the evolutions, since the entropies of the states that are represented in equations (1) and (2) are assumed to be well defined.

Under normal macroscopic conditions, the relation (3) expresses an equality between enormous numbers, if not the trivial relationship $V_{\mathbf{I}} = V_{\mathbf{II}}$ is the case. Therefore, it does not seem possible to verify the formula experimentally. In the present article, a theoretical verification will instead be reached through an alternative derivation of equation (3).

2 Derivation for non-overlapping volumes

Let $V_{\mathbf{I}}$ and $V_{\mathbf{II}}$ denote two arbitrary volumes in an isolated system. If there are additional volumes contained in the system, no molecules are moving in or out of them in the evolutions described below. Assume that $V_{\mathbf{I}}$ and $V_{\mathbf{II}}$ are composed of smaller, equally sized volume cells, $V_{\mathbf{I},i}$ and $V_{\mathbf{II},j}$ such that

$$\begin{aligned} V_{\mathbf{I},1} = V_{\mathbf{I},2} = V_{\mathbf{I},3} = \ldots = V_{\mathbf{I},n} &= \frac{V_{\mathbf{I}}}{n} \\ = V_{\mathbf{II},1} = V_{\mathbf{II},2} = V_{\mathbf{II},3} = \ldots = V_{\mathbf{II},m} &= \frac{V_{\mathbf{II}}}{m} , \end{aligned} \tag{4}$$

which implies

$$V_{\mathbf{I}} = V_{\mathbf{I},1} + V_{\mathbf{I},2} + V_{\mathbf{I},3} + \ldots + V_{\mathbf{I},n} . \tag{5}$$

and

$$V_{\mathbf{II}} = V_{\mathbf{II},1} + V_{\mathbf{II},2} + V_{\mathbf{II},3} + \ldots + V_{\mathbf{II},m} . \tag{6}$$

Moreover, assume that the transition probabilities of single molecules are characterized by microscopic reversibility, in the sense that every transition between two equally sized volume cells has the same time translation invariant future-directed probability (i.e. a probability where

the condition precedes the outcome) in both directions, irrespective of when it takes place and irrespective of the time interval between the two positions. Then, as a consequence of T-invariance, the following relation holds for arbitrary such volume cells:[1]

$$p_1(V_{\mathbf{II},j}[t_1+\tau]|V_{\mathbf{I},i}[t_1]) = p_1(V_{\mathbf{I},i}[t_2+\tau]|V_{\mathbf{II},j}[t_2])\ , \tau > 0. \tag{7}$$

where p_1 denotes that the transition probabilities concerns single molecules.

It is worth noting that the symmetry, represented by equation (7), is time asymmetric in itself, since it describes a relation between two future-directed probabilities, i.e. conditional probabilities where the condition precede the outcome. Equation (7) can be seen as a direct consequence of the *physical symmetry*[2] of the molecules and the *law of statistical time asymmetry*, formulated by Skoruppa (2022a).

Furthermore, assume that the system is in a state of equilibrium at t_0, which means that a randomly chosen molecule contained in $V_{\mathbf{I}}$ has equal probability of being in each of the n cells of $V_{\mathbf{I}}$ at t_0. Thus,

$$p_1(V_{\mathbf{I},i}[t_0]) = \frac{p_1(V_{\mathbf{I}}[t_0])}{n}\ . \tag{8}$$

Now, let $p_1(V_{\mathbf{II},i}[t_0+\tau]|V_{\mathbf{I},i}[t_0])$ denote the probability of a single molecule to move from $V_{\mathbf{I}}$ to $V_{\mathbf{II}}$ during the time interval $[t_0, t_0+\tau]$. For disjoint elements $\{B_1, B_2, B_3, \ldots, B_n\}$, elementary probability theory yields:

$$\begin{aligned} p(A \wedge \{B_1 \vee B_2 \vee B_3 \vee \ldots \vee B_n\}) = p\left(\bigcup_{i=1}^{n} A \wedge B_i\right) &= \{\text{axiom}\} \\ &= \sum_{i=1}^{n} p(A \wedge B_i)\ . \end{aligned} \tag{9}$$

It is now possible to derive the probability of an evolution of a single

[1] This is what Holster (2003) calls *the orthodox criterion for reversal symmetry*. The relations between different time dependent probabilistic symmetries are described in Skoruppa (2022c).

[2] The concept of physical symmetry, well described by Strevens (1998) under the name of *non-enumerative induction*, is not to be confused with *the principle of indifference*.

molecule from $V_{\mathbf{I}}$ to $V_{\mathbf{II}}$ during the time interval $[t_0, t_0+\tau]$, where $\tau > 0$:

$$
\begin{aligned}
& p_1(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0]) = \{\text{definition}\} \\
&= \frac{p_1(V_{\mathbf{II}}[t_0+\tau] \wedge V_{\mathbf{I}}[t_0])}{p(V_{\mathbf{I}}[t_0])} = \{(5)\} = \\
&= \frac{p_1(V_{\mathbf{II}}[t_0+\tau] \wedge \{V_{\mathbf{I},1} \vee V_{\mathbf{I},2} \vee \ldots \vee V_{\mathbf{I},n}[t_0]\})}{p(V_{\mathbf{I}}[t_0])} = \{(9)\} \\
&= \frac{\sum_{i=1}^{n} p_1(V_{\mathbf{II}}[t_0+\tau] \wedge V_{\mathbf{I},\mathbf{i}}[t_0])}{p(V_{\mathbf{I}}[t_0])} = \{(6)\} \\
&= \frac{\sum_{i=1}^{n} p_1(\{V_{\mathbf{II},1} \vee V_{\mathbf{II},2} \vee \ldots \vee V_{\mathbf{II},m}[t_0+\tau]\} \wedge V_{\mathbf{I},i}[t_0])}{p(V_{\mathbf{I}}[t_0])} = \{(9)\} \\
&= \frac{\sum_{i=1}^{n}\sum_{j=1}^{m} p_1(V_{\mathbf{II},j}[t_0+\tau] \wedge V_{\mathbf{I},\mathbf{i}}[t_0])}{p(V_{\mathbf{I}}[t_0])} = \{(8)\} \\
&= \frac{\sum_{i=1}^{n}\sum_{j=1}^{m} p_1(V_{\mathbf{II},j}[t_0+\tau] \wedge V_{\mathbf{I},\mathbf{i}}[t_0])}{n \cdot p(V_{\mathbf{I},i}[t_0])} = \{\text{definition}\} \\
&= \frac{1}{n}\sum_{i=1}^{n}\sum_{j=1}^{m} p_1(V_{\mathbf{II},j}[t_0+\tau]|V_{\mathbf{I},\mathbf{i}}[t_0]) \,. \qquad (10)
\end{aligned}
$$

The probability of the reversed evolution of a single molecule can be derived in a corresponding way. Thus,

$$
p_1(V_{\mathbf{I}}[t'_0+\tau]|V_{\mathbf{II}}[t'_0]) = \frac{1}{m}\sum_{i=1}^{n}\sum_{j=1}^{m} p_1(V_{\mathbf{I},i}[t'_0+\tau]|V_{\mathbf{II},\mathbf{j}}[t'_0]) \,, \tau > 0. \quad (11)
$$

Equations (10) and(11) combine to, given that $\tau > 0$,

$$
\begin{aligned}
\frac{p_1(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p_1(V_{\mathbf{I}}[t'_0+\tau]|V_{\mathbf{II}}[t'_0])} &= \frac{\frac{1}{n}\sum_{i=1}^{n}\sum_{j=1}^{m} p_1(V_{\mathbf{II},j}[t_0+\tau]|V_{\mathbf{I},\mathbf{i}}[t_0])}{\frac{1}{m}\sum_{i=1}^{n}\sum_{j=1}^{m} p_1(V_{\mathbf{I},i}[t'_0+\tau]|V_{\mathbf{II},\mathbf{j}}[t'_0])} = \{(7)\} \\
&= \frac{m}{n} = \{(4)\} \\
&= \frac{V_{\mathbf{II}}}{V_{\mathbf{I}}} \,. \qquad (12)
\end{aligned}
$$

The derivation of equation (3) in the special case where $V_{\mathbf{I}}$ and $V_{\mathbf{II}}$ are non-overlapping can now be accomplished (with N again denoting the number of molecules):

$$\frac{p_N(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p_N(V_{\mathbf{I}}[t_0'+\tau]|V_{\mathbf{II}}[t_0'])} = \frac{\left[p_1(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])\right]^N}{\left[p_1(V_{\mathbf{I}}[t_0'+\tau]|V_{\mathbf{II}}[t_0'])\right]^N} = \{(12)\}$$
$$= \left(\frac{V_{\mathbf{II}}}{V_{\mathbf{I}}}\right)^N, \tau > 0. \tag{13}$$

It should be noted that the derivation is based on the assumption that the gas system is in equilibrium at the *initial* points in time, t_0 and t_0', while it is not necessary that the system is in equilibrium at the final points in time, $t_0+\tau$ and $t_0'+\tau$.

3 Derivation for overlapping volumes

Equation (13), derived in the previous section, describes the relation between probabilities for two evolutions that both are extremely improbable in macroscopic systems, and they are therefore in practice non-physical. An evolution, which on the contrary is feasible, is a gas that expands from a small volume into an empty larger volume, where the latter includes the former.

It is possible to derive the relation between the future-directed probabilities of this type of evolution and its time-reversed counterpart on the basis of equation (13). Assume that two non-overlapping volumes, $V_{\mathbf{I}}$ and $V_{\mathbf{A}}$, are connected with each other in an isolated system, so that the contained gas molecules can pass freely between the volumes. Moreover, assume that a third volume $V_{\mathbf{II}}$ is defined as a part of the volume $V_{\mathbf{I}}$, such that $V_{\mathbf{II}} < V_{\mathbf{I}}$.

Then, according to equation (13):

$$\frac{p(V_{\mathbf{I}}[t_1+\tau]|V_{\mathbf{A}}[t_1])}{p(V_{\mathbf{A}}[t_2+\tau]|V_{\mathbf{I}}[t_2])} = \left(\frac{V_{\mathbf{I}}}{V_{\mathbf{A}}}\right)^N, \tau > 0, \tag{14}$$

and

$$\frac{p(V_{\mathbf{A}}[t_3+\tau]|V_{\mathbf{II}}[t_3])}{p(V_{\mathbf{II}}[t_4+\tau]|V_{\mathbf{A}}[t_4])} = \left(\frac{V_{\mathbf{A}}}{V_{\mathbf{II}}}\right)^N, \tau > 0. \tag{15}$$

Assume that all molecules are in a state of local equilibrium in the volume in question. Furthermore, assume that the system is free from circular probability currents, i.e. is characterized by detailed balance,

and thus (for arbitrary points in time t_0, t_0', t_1, t_2, t_3, and t_4 and for $\tau > 0$),

$$\begin{aligned}
&p(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0]) \cdot p(V_{\mathbf{I}}[t_1+\tau]|V_{\mathbf{A}}[t_1]) \cdot p(V_{\mathbf{A}}[t_3+\tau]|V_{\mathbf{II}}[t_3]) \\
&\quad = p(V_{\mathbf{I}}[t_0'+\tau]|V_{\mathbf{II}}[t_0']) \cdot p(V_{\mathbf{A}}[t_2+\tau]|V_{\mathbf{I}}[t_2]) \cdot p(V_{\mathbf{II}}[t_4+\tau]|V_{\mathbf{A}}[t_4]) \\
\Rightarrow\ &\frac{p(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p(V_{\mathbf{I}}[t_0'+\tau]|V_{\mathbf{II}}[t_0'])} \cdot \frac{p(V_{\mathbf{I}}[t_1+\tau]|V_{\mathbf{A}}[t_1])}{p(V_{\mathbf{A}}[t_2+\tau]|V_{\mathbf{I}}[t_2])} \cdot \frac{p(V_{\mathbf{A}}[t_3+\tau]|V_{\mathbf{II}}[t_3])}{p(V_{\mathbf{II}}[t_4+\tau]|V_{\mathbf{A}}[t_4])} = 1 \\
\Rightarrow\ &\{(14),(15)\} \\
\Rightarrow\ &\frac{p(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p(V_{\mathbf{I}}[t_0'+\tau]|V_{\mathbf{II}}[t_0'])} = \left(\frac{V_{\mathbf{A}}}{V_{\mathbf{I}}}\right)^N \cdot \left(\frac{V_{\mathbf{II}}}{V_{\mathbf{A}}}\right)^N \\
\Rightarrow\ &\frac{p(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p(V_{\mathbf{I}}[t_0'+\tau]|V_{\mathbf{II}}[t_0'])} = \left(\frac{V_{\mathbf{II}}}{V_{\mathbf{I}}}\right)^N, \tau > 0. \qquad (16)
\end{aligned}$$

If volume V_A is assumed to be infinitesimal small, i.e. $\lim_{V_A \to 0}$, equation (16) describes a relation between the future-directed probabilities of a freely expanding ideal gas that evolves between a smaller and a larger volume, where the former is a part of the latter, i.e. when the volumes are overlapping. This formula is identical to equation (3) and is therefore a confirmation of the derivation in Skoruppa (2022b, Section 7).

4 Conclusions

Since the derivations in the previous sections include both cases where the volumes in question are overlapping and when they are not, the resulting formula can be considered generally describing the evolution of molecules in an ideal gas between two volumes:

$$\frac{p(V_{\mathbf{II}}[t_0+\tau]|V_{\mathbf{I}}[t_0])}{p(V_{\mathbf{I}}[t_0'+\tau]|V_{\mathbf{II}}[t_0'])} = \left(\frac{V_{\mathbf{II}}}{V_{\mathbf{I}}}\right)^N, \tau > 0, \qquad (17)$$

where t_0 and t_0' are points in time when the molecules in $V_{\mathbf{I}}$ and $V_{\mathbf{II}}$, respectively, are in a state of equilibrium, and τ is an arbitrary positive time interval.

According to the derivations in Sections 2 and 3, equation (17) holds under the conditions that

- the system containing the volumes in question is isolated, and
- the system is in equilibrium at the beginning of the evolutions,

and given the assumptions that

- the microscopic evolution of single molecules is reversible,

- only the future-directed probabilities are time translation invariant in accordance with *the law of statistical time asymmetry*, and

- there are no circular probability currents (i.e. the statistical evolution meets the criteria for detailed balance).

The condition of isolation as well as the concepts of an ideal gas and an infinitesimal small volume are idealizations, which the derivations are built upon. However, it is reasonable to conclude that the formula (17) holds with a high degree of accuracy in a realistic gas system.

The derivation in Section 3 results in an equation that is identical to equation (3). Since the latter equation is based on the *statistical entropy difference* formula, the alternate derivation in the present article can be considered as a partly verification of that formula.

References

Holster, A. (2003). The criterion for time symmetry of probabilistic theories and the reversibility of quantum mechanics. *New Journal of Physics*, 5, 130.1–130.28.

Skoruppa, B. (2022a). A proposed law for statistical time asymmetry. Appendix II.

Skoruppa, B. (2022b). Statistical entropy difference. Appendix VIII.

Skoruppa, B. (2022c). Time reversal invariance and asymmetry in probability based laws. Appendix I.

Strevens, M. (1998). Inferring probabilities from symmetries. *Nôus*, 32, 231–246.