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Appendix IV. Derivation of rate equations from time-directed probabilities of individual particles

Abstract

The time asymmetry in macroscopic systems is hypothesized to have its foundation in time-directed probabilities of microscopic origin. To make way for a general description of physical time asymmetry, large-scale consequences of composite systems are derived from a proposed law that establishes a statistical time asymmetry at the microscopic level. The derivations are made for radioactive decay, expanding gas and bimolecular chemical reaction. The derivations result in rate equations describing the macroscopic evolution of the systems, which constitute a verification of the proposed law, since they are in accordance with empirical facts.

1 Introduction

Efforts have been made for a long time to bridge the gap between the time symmetry in mechanical laws ruling microscopic processes and the time asymmetry characterizing many macroscopic processes. Rain falls down, people are getting older, and stars are burnt out, while the fundamental mechanical laws do not make any corresponding difference between the past and future time direction. Thus, there seems to be a need for a general description of time asymmetry that embraces both microscopic and macroscopic levels.

A possible hypothesis would be the existence of a qualitative difference between the microscopic and macroscopic levels, where the time asymmetry emerges somewhere between these levels. However, it is hard to imagine a theory prescribing a reasonable constitution of such a shift between microscopic and macroscopic phenomena. Therefore, in this article it will instead be hypothesized that there exists lawlike time asymmetries on both levels, and that these asymmetries are direct consequences of the *law of statistical time asymmetry*, recently formulated by Skoruppa (2022b).

According to the Law of Stability of Relative Frequencies, a composite system has a tendency to show a kind of quasi-deterministic behaviour, even though the individual systems are behaving randomly. For example, if 6000 dice are thrown, predictably between 900 and 1100 will show sixes, even though every single die is unpredictable. And if something tears a hole in a bicycle tyre, the tyre will predictably get flat, even if the behaviour of the individual gas molecules is unpredictable. This property of randomness is aptly described by the philosopher Mario Bunge (1999, p. 83) as a "particular kind of disorder characterized by local irregularity (e.g., individual coin tossing) combined with global regularity (e.g., long-run chances of heads and tails)."

A reasonable hypothesis, given this property of randomness, is that there exists a statistical time asymmetry at the level of individual events, occasionally giving rise to a quasi-deterministic time asymmetric evolution at the composite level. To test this hypothesis, the present article aims to analyse the consequences of a hypothesized statistical time asymmetry for composite systems consisting of a special kind of stochastic evolution at the individual level, termed *continuous-time Markov processes.* This kind of process is assumed to have "'no memory' but also 'no foresight'",[1] implying that the conditional transition probabilities governing the process only depend on the condition on the instance that is temporally closest in either the past or the future.

Examples of physical phenomena, the evolutions of which are very close to being Markov processes, are decaying radioactive atoms, photon emissions from excited atoms and dissolving chemical bonds. However, the assumption that these are Markov processes is only approximately correct, since quantum theory prescribes that the probability of an unstable quantum system to leave its state depends on the time interval that has passed since the last measurement. Fortunately, the deviation is negligible except for extremely short time intervals after a completed measurement.[2]

Markov processes can also be found in models of physical processes, for example the transfer of balls in the urn model, introduced by Paul and Tatiana Ehrenfest (1907), where they, however, are not continuous-time. The aim of the present article is to derive quasi-deterministic *macroscopic* time asymmetry from probabilistic *microscopic* time asymmetry in accordance with the *law of statistical time asymmetry* in three types of processes that are assumed to behave as continuous-time Markov processes. In other words, these derivations of macroscopic evolution are made on the basis of time asymmetric assumptions on the microscopic level.[3]

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[1] Uffink (2007, p. 126).

[2] Khalfin (1958) and Greenland (1988) describe the time dependence of radioactive decay.

[3] This approach contrasts with what te Vrugt (2021) describes: "In physics, derivations of irreversible equations from the reversible microscopic physics have a long tradition, starting from Boltzmanns H-theorem discussed in section 3."

2 A proposed law to be verified

In a previous article (Skoruppa, 2022b) the following physical law was proposed to establish a general time asymmetry in systems that can be correctly described by time translation invariant probabilities ($A[t_1, t_2]$ and $B[t_3, t_4]$ denote states or processes of a given system during the given time intervals):[4]

> **Law of statistical mechanical time asymmetry**
> Assume that $A[t_1, t_2]$ and $B[t_3, t_4]$, where $t_1 \leq t_2 \leq t_3 \leq t_4$ and $t_1 < t_4$, are macroscopic states, defined by the same quantities and the same degree of coarse graining in an isolated disequilibrium process. Then $p(B[t_3, t_4]|A[t_1, t_2])$ is always, while $p(A[t_1, t_2]|B[t_3, t_4])$ is never, time translation invariant through the entire evolution from disequilibrium to an enduring equilibrium.

The two kinds of conditional probabilities in the law can be defined in the following ways.

Definition 1 *Future-directed probability:*

$$p(B[t_3, t_4]|A[t_1, t_2]) = \frac{p(A[t_1, t_2] \wedge B[t_3, t_4])}{p(A[t_1, t_2])} \ ,$$

where $t_1 \leq t_2 \leq t_3 \leq t_4$ and $t_1 < t_4$.

Definition 2 *Past-directed probability:*

$$p(A[t_1, t_2]|B[t_3, t_4]) = \frac{p(A[t_1, t_2] \wedge B[t_3, t_4])}{p(B[t_3, t_4])} \ ,$$

where $t_1 \leq t_2 \leq t_3 \leq t_4$ and $t_1 < t_4$.

To perform the derivations in Sections 3, 4, and 5, a version of the frequency interpretation of conditional probability, adopted for this purpose, is needed:

$$p(Y[t + \Delta t]|X[t]) = \lim_{n \to \infty} \frac{n(X[t] \wedge Y[t + \Delta t])}{n(X[t])} = \frac{n_e(X[t] \wedge Y[t + \Delta t])}{n_e(X[t])} \ , \tag{1}$$

where n_e denotes *expected* frequency, given boundary conditions and the ruling probabilities, and where t and $t + \Delta t$ denote points in time of the states X and Y, respectively. Δt denotes a *positive* time interval here as well as in the rest of the present article.

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[4] This is the statistical mechanical version of the more general *law of statistical time asymmetry* that is presented in Skoruppa (2022b).

The three derivations in Sections 3, 4, and 5 are made on the basis of the assumption that the evolution of the individual disequilibrium processes can be correctly described by *future-directed* probabilities that are time translation invariant. This implies, according to a proof by Sober (1993), that these systems cannot be correctly described by *past-directed* probabilities that are time translation invariant. Sober's proof shows that a process cannot be correctly described by both kinds of time-directed probabilities if

- the expected state of the system changes with time,
- the time-directed transition probabilities in at least one time-direction are time translation invariant,
- not all of the time-directed transition probabilities are 0 or 1,
- there is a nonzero probability for the system to maintain its state,
- the system has finitely many states.[5]

So if the derivations, based on the future-directed probabilities of individual particles, result in macroscopic descriptions that are in harmony with empirical findings for the three phenomena in question, and if the phenomena meet the criteria above, they cannot be correctly described by time translation invariant past-directed probabilities according to the proof by Sober (1993). If this turns out to be the case, the following derivations can therefore be considered to verify the *law of statistical mechanical time asymmetry.*

3 Derivation of a first order rate equation on the basis of time-directed probabilities

The expected evolution of a group of radioactive atoms in a large reservoir with no production of such atoms is analysed in this section. As a starting-point the following notation is established.

R: an atom in a radioactive state.

D: a radioactive atom in a decayed state with adherent decay products.

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[5] Arntzenius (1997) has made a proof that aims to imply conclusions similar to those made by Sober (1993) for *processes approaching equilibrium*, and which is applicable to systems with an infinite number of states. Therefore, if Arntzenius's proof is correct, which the present writer is not skilled enough to decide, the last criterion is a superfluous condition for the derivations in the present article.

$X[t]$: a microscopic system registered in state X at the point in time t.

$X[t, t+\Delta t]$: a microscopic system maintains its state X during the closed time interval between t and $t+\Delta t$, where $\Delta t \geq 0$.[6]

$n_e(X[t])$: the expected number of microscopic systems in state X at t.

$n_e(X[t] \wedge Y[t+\Delta t])$: the expected number of microscopic systems evolving from state X to state Y in the closed time interval between t and $t+\Delta t$, where $\Delta t \geq 0$.

The radioactive atoms are assumed not to interact with each other or with the environment.[7] As a consequence, an atom, being in a state of radioactivity (i.e. disequilibrium) at t, is either radioactive in the whole interval $[t, t+\Delta t]$ or is in a decayed (i.e. an equilibrium) state at $t+\Delta t$. Thus, the following relation between two future-directed probabilities holds:

$$p(R[t, t+\Delta t]|R[t]) + p(D[t+\Delta t]|R[t]) = 1 \ . \tag{2}$$

Radioactive decay is assumed to have negligible deviation from a continuous-time Markov process that can be correctly described by conditional probabilities that are time translation invariant, in accordance with the line of reasoning in Section 1. Moreover, the future-directed probability of a radioactive atom to maintain its radioactive state in the time interval $[t, t+\Delta t]$ is assumed to be time translation invariant in accordance with the *law of statistical mechanical time asymmetry.* According to Skoruppa (2022a),[8] this implies

$$p(R[t, t+\Delta t]|R[t]) = e^{-\lambda \cdot \Delta t} \ , \quad \lambda > 0 \ . \tag{3}$$

Furthermore, since $n_e(R[t])$ denotes the *expected* number of atoms, according to the notation at the beginning of this section, it is assumed to be a continuous function with a well defined derivative:

$$\frac{d}{dt} n_e(R[t]) = \lim_{\Delta t \to 0} \frac{n_e(R[t+\Delta t]) - n_e(R[t])}{\Delta t} \ . \tag{4}$$

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[6] This is a classical description and, therefore, the particles are assumed to have unambiguous positions between measurements.

[7] It can be questioned if the decay process really is isolated, since the decay products are assumed to move into some kind of reservoir. Therefore, the wider *law of general statistical time asymmetry*, defined in Skoruppa (2022c), could be more suitable as a point of departure in the derivation of macroscopic time asymmetry in the decay processes. However, this would not change the present analysis in essence.

[8] The same formula, without the notation of time-directed probabilities, can be found in Meyer & Schweidler (1915).

The difference in the expected amount of R in equation (4) equals the negative of the expected unidirectional flow of the evolutions $R \to D$, and therefore

$$\begin{aligned}\frac{d}{dt} n_e(R[t]) &= \lim_{\Delta t \to 0} \frac{-n_e(R[t] \wedge D[t+\Delta t])}{\Delta t} = \{(1)\}\\ &= \lim_{\Delta t \to 0} \frac{-n_e(R[t]) \cdot p(D[t+\Delta t] | R[t])}{\Delta t} = \{(2)\}\\ &= \lim_{\Delta t \to 0} -\frac{1 - p(R[t, t+\Delta t] | R[t])}{\Delta t} \cdot n_e(R[t]) = \{(3)\}\\ &= \lim_{\Delta t \to 0} -\frac{1 - e^{-\lambda \cdot \Delta t}}{\Delta t} \cdot n_e(R[t]) = \{\text{l'Hospital's rule}\}\\ &= -\lambda \cdot n_e(R[t]) \ .\end{aligned}$$

This represents a rate equation in the form of a separable differential equation, which is limited by the inequality (3). Since λ is a constant, the following solution is implied:

$$n_e(R[t]) = n_e(R[0]) \cdot e^{-\lambda \cdot t} \ , \quad \lambda > 0 \ .$$

This is the experimentally well-founded equation of time asymmetric radioactive decay, and consequently the derivation above is empirically verified.

It can easily be shown that the radioactive decay process meet the five criteria in the end of Section 2. As noted in the same section, all of this means, according to the proof by Sober (1993), that a correct derivation of the radioactive decay process cannot be made on the basis of time translation invariant *past-directed* probabilities. Therefore, the derivation above, which describes the evolution from a state of radioactive disequilibrium to a state of decayed equilibrium, is also a verification of the *law of statistical mechanical time asymmetry.*

4 Derivation of an disequilibrium process rate equation on the basis of time-directed probabilities

Consider the expected evolution of expanding gas in a closed container divided in two vessels, A and B, with a hole between them. The molecules in each vessel are assumed to be evenly distributed and the temperature is assumed to be constant. In order to limit the influence of the collisions, the pressure of the gas is assumed to be comparatively low. In addition to the notation at the beginning of Section 3, the following notation is established.

A: a certain molecule situated in vessel A.

B: a certain molecule situated in vessel B.

The transfer of a molecule from vessel A to vessel B and vice versa in an ideal gas is assumed to be a continuous-time Markov process that can be correctly described by time translation invariant conditional probabilities. Moreover, the future-directed probabilities, both for a molecule to maintain its state A and its state B in the time interval $[t, t+\Delta t]$, where $\Delta t > 0$, are assumed to be time translation invariant in accordance with the *law of statistical mechanical time asymmetry.*

The assumption that the molecules are evenly distributed in their respective vessels implies that the probability of a molecule passage from one of the vessels is proportional to the density of the molecules in that vessel, given that the future-directed probabilities are time translation invariant. Macroscopically, this is equivalent to the assumption that each molecule in respective vessel has the same probability of passing through the hole. For the sake of simplicity, the latter assumption is considered valid from now on. According to the conclusions in Skoruppa (2022a), this implies[9]

$$p(A[t, t+\Delta t]|A[t]) = e^{-a\cdot\Delta t}\ , \quad a > 0\ ; \tag{5}$$

$$p(B[t, t+\Delta t]|B[t]) = e^{-b\cdot\Delta t}\ , \quad b > 0\ . \tag{6}$$

A molecule either still is in the same vessel after the interval $[t, t+\Delta t]$ or is transferred to the other vessel at $t+\Delta t$. Therefore, the following two relations between future-directed probabilities holds:

$$p(A[t, t+\Delta t]|A[t]) + p(B[t+\Delta t]|A[t]) = 1\ . \tag{7}$$

and

$$p(B[t, t+\Delta t]|B[t]) + p(A[t+\Delta t]|B[t]) = 1\ . \tag{8}$$

Since there is less and less time for a molecule to pass through the hole more than once as $\lim_{\Delta t\to 0}$, the probability of a single passage in a certain direction is assumed to be the same as the probability of a passage in the same direction that *possibly* is followed by further passages, given $\lim_{\Delta t\to 0}$. Therefore, the following two relations are assumed to

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[9] According to Skoruppa (2022a), Section 4, 1/a and 1/b are the average time intervals that the molecule spends in A and B, respectively, before they change vessel. Since these time intervals must be inversely proportional to the volumes, V_A and V_B, $a = k/V_A$ and $b = k/V_B$.

hold:[10]

$$\lim_{\Delta t\to 0} p(A[t+\Delta t]|A[t]) = \lim_{\Delta t\to 0} p(A[t,t+\Delta t]|A[t])\ , \text{ and} \tag{9}$$

$$\lim_{\Delta t\to 0} p(B[t+\Delta t]|B[t]) = \lim_{\Delta t\to 0} p(B[t,t+\Delta t]|B[t])\ . \tag{10}$$

Since $n_e(A[t])$ denotes the *expected* number of molecules, according to the notation in the beginning of Section 3, it is assumed to be a continuous function with a well defined derivative:

$$\frac{d}{dt} n_e(A[t]) = \lim_{\Delta t\to 0} \frac{n_e(A[t+\Delta t]) - n_e(A[t])}{\Delta t}\ . \tag{11}$$

The difference in the expected amount of A in equation (11) equals the expected net flow of the evolutions of $B \to A$, and therefore

$$\begin{aligned}
&\frac{d}{dt} n_e(A[t])\\
&= \lim_{\Delta t\to 0} \frac{n_e(B[t]\wedge A[t+\Delta t]) - n_e(A[t]\wedge B[t+\Delta t])}{\Delta t} = \{(1)\}\\
&= \lim_{\Delta t\to 0} \frac{n_e(B[t])\cdot p(A[t+\Delta t]|B[t])}{\Delta t} - \frac{n_e(A[t])\cdot p(B[t+\Delta t]|A[t])}{\Delta t}\\
&=\{(7),(8)\}\\
&= \lim_{\Delta t\to 0} \frac{n_e(B[t])\cdot [1 - p(B[t+\Delta t]|B[t])]}{\Delta t}\\
&\qquad\qquad - \frac{n_e(A[t])\cdot [1 - p(A[t+\Delta t]|A[t])]}{\Delta t} = \{(9),(10)\}\\
&= \lim_{\Delta t\to 0} n_e(B[t])\cdot \frac{1 - p(B[t,t+\Delta t]|B[t])}{\Delta t}\\
&\qquad\qquad - n_e(A[t])\cdot \frac{1 - p(A[t,t+\Delta t]|A[t])}{\Delta t} = \{(5),(6)\}\\
&= \lim_{\Delta t\to 0} n_e(B[t])\cdot \frac{1-e^{-b\cdot\Delta t}}{\Delta t} - n_e(A[t])\cdot \frac{1-e^{-a\cdot\Delta t}}{\Delta t} =\\
&= \{\text{l'Hospital's rule}\} =\\
&= b\cdot n_e(B[t]) - a\cdot n_e(A[t])\ .
\end{aligned}$$

This represents a rate equation that can be transformed into a separable differential equation by letting $n_{tot} = n_e(A[t]) + n_e(B[t]) \Rightarrow n_e(B[t])$ denote the total number of molecules, which is constant since the container is closed:

$$\begin{aligned}
\frac{d}{dt} n_e(A[t]) &= b\cdot (n_{tot} - n_e(A[t]) - a\cdot n_e(A[t])\\
&= -(a+b)\cdot n_e(A[t]) + b\cdot n_{tot}\ .
\end{aligned}$$

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[10] This assumption ought to be put on a more solid theoretical ground, but the present author was not capable of deriving equation (9) and (10), which therefore are postulated.

The differential equation has the following solution, with limits implied by (5) and (6):

$$n_e(A[t]) = n_{A,eq} + (n_A[0] - n_{A,eq}) \cdot e^{-(a+b)\cdot t} \ , \quad a > 0, b > 0 \ , \qquad (12)$$

where $n_{A,eq} = \lim_{t\to\infty} n_e(A[t]) = \frac{b}{a+b} \cdot n_{tot}$, and $n_A[0]$ is the initial number of molecules in vessel A. This result both describes the disequilibrium process and the transition to equilibrium and can be compared with empirical findings to find out whether the derivation is based on the correct assumptions. A clue that this is true is that equation (12) correctly describes the statistically expected evolution of Ehrenfest's urn model, if $a = b$.[11]

Since the gas process meets the criteria in the end of Section 2, such a verification would mean, according to the proof of Sober (1993), that the correct derivation cannot be made on the basis of time translation invariant *past-directed* probabilities for an expanding ideal gas. Therefore, a verification of the derivation above would also be a verification of the *law of statistical mechanical time asymmetry.*

5 Derivation of a second order rate equation on the basis of time-directed probabilities

Now, consider a bimolecular reaction, in which two identical molecules of a given substance form a number of other kinds of molecules (the empirical example $2NO_2 \to 2NO + O_2$ is given in the end of this section):

$$2E \to \neg E \ .$$

A large amount of E molecules are assumed to be evenly distributed, and both the temperature and the solution volume are assumed to be constant.[12] In addition to the notation in the beginning of Section 3, the following notation is established:

$2E$: two molecules of the substance E.

$\neg E$: particles, earlier in the shape of two E molecules, transformed to some other form of matter as a result of a chemical reaction.

$\bar{t}_E[t]$: the average time before an E molecule transforms to $\neg E$, as a function of time.

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[11] Ehrenfest & Ehrenfest (1907). The derivation in the case of the urn model turns out to be somewhat different, since the time evolution in the model is discrete, but it will not be shown here.

[12] Normally, in chemical kinetics, the rate equations deal with functions measuring the *concentration* of the substance rather than the number of particles, but in the present article the *number* is preferred in order to make the derivations in the different sections concordant.

The reversed evolution $\neg E \to 2E$ is assumed to be negligible. Since the evolution thereby is assumed to be unidirectional, an E molecule at t must either maintain its state during the whole interval $[t, t + \Delta t]$, or they are in the state $\neg E$ at $t + \Delta t$. Therefore, the following relation between two future-directed probabilities holds:

$$p(2E[t, t + \Delta t]|2E[t]) + p(\neg E[t + \Delta t]|2E[t]) = 1 \; . \tag{13}$$

The derivation of a time-dependent probability function for the reaction $2E \to \neg E$ is not straightforward, since the assumption that the evolution of two E molecules is time translation invariant can only be expected to be valid if the concentration of E molecules is constant. If this concentration varies, the probability for a certain E molecule to collide with another molecule of the same kind – which is necessary for a reaction – presumably decreases when the concentration of E molecules sinks.

As a first step towards a probability function, the evolution of two E molecules is analysed with respect to an environment having a constant number, $n_e(E[t]) = n_E$, of such molecules, which implies that they have a constant concentration. The chemical reaction of a molecule in state E with another molecule of the same kind, is assumed to be a continuous-time Markov process that can be correctly described by conditional probabilities that are time translation invariant. Under this condition, the future-directed probability for an E molecule to maintain its state during the time interval $[t, t + \Delta t]$ is assumed to be time translation invariant in accordance with the *law of statistical mechanical time asymmetry*. According to the conclusions in Skoruppa (2022a), this implies

$$p(2E[t, t + \Delta t]|2E[t]) = e^{-\Delta t/\bar{t}_E} \; , \quad \bar{t}_E > 0 \; . \tag{14}$$

Reasonably, the average time, $\bar{t}_E[t] = \bar{t}_E$, before a certain E molecule reacts with another E molecule is in inverse proportion to the concentration of E molecules in the solution. And since the concentration of molecules is proportional to the number of molecules in the solution, $n_e(E[t])$, the average time before a certain molecule reacts with another E molecule is assumed to be in inverse proportion to $n_e(E[t])$:

$$\frac{1}{\bar{t}_E[t]} = k \cdot n_e(E[t]) \; . \tag{15}$$

The next step is to describe the probability function (14) when the expected number of E molecules, $n_e(E[t]))$, varies with time. The proportionality given by equation (15) is assumed to be valid also when the concentration of molecules is variable, and thus:

$$\{(14), (15)\} \Rightarrow \; p(2E[t, t + \Delta t]|2E[t]) = e^{-k \cdot n_e(E[t]) \cdot \Delta t}, \; k > 0 \; . \tag{16}$$

Since $n_e(E[t])$ denotes the *expected* number of molecules, according to the notation in Section 3, it is assumed to be a continuous function with a well defined derivative:

$$\frac{d}{dt} n_e(E[t]) = \lim_{\Delta t \to 0} \frac{n_e(2E[t+\Delta t]) - n_e(2E[t])}{2 \cdot \Delta t} , \tag{17}$$

where the number 2 in the denominator follows since two molecules transform during each single reaction.

The difference in the expected amount of E in equation (17) equals the negative of the expected unidirectional flow of the evolutions $2E \to \neg E$, and therefore

$$\begin{aligned}
\frac{d}{dt} n_e(E[t]) &= \lim_{\Delta t \to 0} \frac{-n_e(2E[t] \wedge \neg E[t+\Delta t])}{2 \cdot \Delta t} = \{(1)\} \\
&= \lim_{\Delta t \to 0} \frac{-n_e(2E[t]) \cdot p(\neg E[t+\Delta t] | 2E[t])}{2 \cdot \Delta t} = \{(13)\} \\
&= \lim_{\Delta t \to 0} -\frac{1 - p(2E[t, t+\Delta t] | 2E[t])}{\Delta t} \cdot \frac{n_e(2E[t])}{2} \\
&= \lim_{\Delta t \to 0} -\frac{1 - p(2E[t, t+\Delta t] | 2E[t])}{\Delta t} \cdot n_e(E[t]) = \{(16)\} \\
&= \lim_{\Delta t \to 0} -\frac{1 - e^{-k \cdot n_e(E[t]) \cdot \Delta t}}{\Delta t} \cdot n_e(E[t]) = \{\text{l'Hospital's rule}\} \\
&= -k \cdot (n_e(E[t]))^2 .
\end{aligned}$$

This represents a rate equation in the form of a separable differential equation that is limited by the inequality $k > 0$, following from equation (16). Since k is a constant, the following solution is implied:

$$n_e(E[t]) = \frac{n_E[0]}{1 + n_E[0]) \cdot k \cdot t} , \quad k > 0 .$$

This is an experimentally well-founded time asymmetric formula for chemical bimolecular reactions, which both describes the disequilibrium process and the transition to equilibrium, for example in the reaction

$$2\mathrm{NO}_2 \to 2\mathrm{NO} + \mathrm{O}_2 .$$

Thus, the derivation above is empirically verified. As concluded in Section 2, this means, according to the proof of Sober (1993), that the correct derivation cannot be made on the basis of time translation invariant *past-directed* probabilities for this kind of chemical reaction. Consequently, the derivation above is also a verification of the *law of statistical mechanical time asymmetry.*

Table 1: Rate equations derived from future-directed probabilities.

Microscopic process	Time translation invariant future-directed probabilities	Rate equation, describing macroscopic time asymmetry
Radioactive decay $R \to \neg R$	$p(R[t, t + \Delta t] \vert R[t]) = e^{-\lambda \cdot \Delta t}$	$\frac{d}{dt} n_e(R[t]) = -\lambda \cdot n_e(R[t])$
Expanding gas $A \rightleftarrows B$	$p(A[t, t + \Delta t] \vert A[t]) = e^{-a \cdot \Delta t}$ $p(B[t, t + \Delta t] \vert B[t]) = e^{-b \cdot \Delta t}$	$\frac{d}{dt} n_e(A[t]) = b \cdot n_e(B[t]) - a \cdot n_e(A[t])$
Chemical reaction $2E \to \neg E$	$p(2E[t, t + \Delta t] \vert 2E[t]) = e^{-k \cdot n_e(E[t]) \cdot \Delta t}$	$\frac{d}{dt} n_e(E[t]) = -k \cdot [n_e(E[t])]^2$

6 Discussion

As becomes clear from a comparison of the analyses in Sections 3, 4, and 5, there are many similarities between the phenomena analysed (Table 1). The three time asymmetric macroscopic evolutions can all be derived from time-directed probabilities at the microscopic level. These probabilities, in their turn, are based on the assumption that the microscopic events are correctly describable as Markov processes with future-directed probabilities that are time translation invariant. Two of the three resulting rate equations are in accordance with empirical findings from experiments involving radioactive decay and chemical reactions, and the remaining rate equation of expanding gas corresponds to a well-known model of this kind of process.

In this way, the present work provides verification of the *law of statistical mechanical time asymmetry*, given in Section 2 and, as a consequence, also of the more general *law of statistical time asymmetry.* This conclusion can be drawn because empirically validated evolutions from disequilibrium to equilibrium, according to the analyses in Sections 3, 4, and 5, can be derived from future-directed probabilities. These probabilities are therefore verified as correct descriptions of the microscopic evolution and this is exactly what the law stipulates.

A common property of the three processes analysed in the present article is the *quasi-deterministic* macroscopic evolution of the composite systems in question, in spite of the microscopic evolution being correctly described by probabilities. There are other phenomena with corresponding features, and the derivations above can be used as models for further exploration. For example, the time evolution of radioactive decay has similar characteristics as excited atoms emitting photons, monomolecular chemical reactions and a ball on a jet of water.[13] Presumably, it is also possible to make derivations of more complex processes governed by probabilities that are time translation invariant. Complicated chemical reactions, series of radioactive decay, or the phenomena of osmosis, thermal conduction, diffusion and convection are examples suitable for investigation.[14]

In conclusion, the analyses and calculations in Sections 3, 4, and 5 have shown that it is possible to derive a macroscopic, quasi-deterministic time asymmetry based on the time-directed probabilities of the individual microscopic events. The common starting-point of these derivations is the assumption that the microscopic events are identical to or close to Markov processes, correctly describable by *future-directed* probabilities that are time translation invariant. This, in turn, implies that the time asymmetries of radioactive decay, expanding gas, and bimolecular chemical reaction can be described as a direct consequence of the *law of statistical time asymmetry.*

References

Arntzenius, F. (1997). Transition chances and causation. *Pacific Philosophical Quarterly*, 78, 149–168.

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[13] The experiment with a ball on a jet of water is described in Skoruppa (2022c).

[14] Uffink (2001) writes:

> There exists, apart from the works of Carnot, Clausius, Kelvin, Gibbs and Planck, another classical tradition in the study of heat phenomena, e.g. the heat equation of Fourier. This equation shows all the aspects one would like to associate with an arrow of time: it contains time explicitly; the class of solutions is not invariant when we replace t by $-t$; they show a clear unidirectional tendency to equalize temperature differences, etc. Similar remarks hold for the diffusion equation of Fick, and other equations describing the macroscopic flow of heat and matter (often collectively called transport equations).
>
> Furthermore, transport equations form a bona fide part of classical physics. The question is then: what is the relation of this tradition to thermodynamics? The answer is rather surprising. Truesdell (1980) observed that in one and a half centuries of their coexistence, not a single work has appeared in which the behaviour of heat, as described by the heat equation, and as described by thermodynamics, are related to each other. One has to conclude that the heat equation and other transport equations simply do not belong to classical thermodynamics!.' (Uffink, 2001, p. 95–96)

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