Relaxation of ideal classical particles in a one-dimensional box

Florian Gebhard* and Kevin zu Münster
Department of Physics, Philipps-Universität Marburg, D-35032 Marburg, Germany

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We study the deterministic dynamics of non-interacting classical gas particles confined to a one-dimensional box as a pedagogical toy model for the relaxation of the Boltzmann distribution towards equilibrium. Hard container walls alone induce a uniform distribution of the gas particles at large times. For the relaxation of the velocity distribution we model the dynamical walls by independent scatterers. The Markov property guarantees a stationary but not necessarily thermal velocity distribution for the gas particles at large times. We identify the conditions for physical walls where the stationary velocity distribution is the Maxwell distribution. For our numerical simulation we represent the wall particles by independent harmonic oscillators. The corresponding dynamical map for oscillators with a fixed phase (Fermi–Ulam accelerator) is chaotic for mesoscopic box dimensions.

1 Introduction

Classical mechanics and electrodynamics, quantum mechanics and quantum field theory are based on a deterministic time evolution. For given initial conditions, the particle positions and velocities or the values of the electromagnetic and Schrödinger fields are known for all times. Therefore, a lecturer of an introductory course on statistical mechanics faces the demanding task to justify a probabilistic description of physical processes on macroscopic time and length scales.

Qualitative arguments which emphasize the importance of the thermodynamic limit are helpful. Students can certainly understand intuitively that information gets lost by destructive interference of individual signals: a man who listens simultaneously to ten thousand discussing philosophers receives as much information as if he was herding a flock of sheep. Nevertheless, it is always helpful to provide explicit calculations for simple examples where the student can explicitly see that the outcome of a measurement on a macroscopic deterministic system can be derived equivalently from the consideration of a probabilistic substitute system.

In this work, we provide such a simple example. We consider a toy model of classical non-interacting point particles in a box. We assume that our initial conditions factorize in the three spatial coordinates. Therefore, without a loss of applicability to three dimensions, we focus on one spatial dimension. We investigate how an initially non-thermal Boltzmann distribution function relaxes to thermal equilibrium for large times. As we develop our model, we shall encounter the known requirements for a stochastic description of a deterministic system, e.g., the coupling of the gas particles to a reservoir. It is the purpose of this work to show step by step how the relaxation of independent point particles is accomplished, without referring to concepts of statistical mechanics such as the entropy or the Boltzmann Stoßzahl Ansatz. For a thorough discussion of one-dimensional models which employ the Boltzmann equation, see Ref. [1].

In Sect.2 we specify the ‘swimming-lane’ model for the particle propagation and the prediction for the Boltzmann distribution from statistical mechanics. In Sect.3 we consider hard walls where the distribution of particle velocities remains constant in time. We show analytically that the particles are homogeneously

* Corresponding author E-mail: florian.gebhard@physik.uni-marburg.de, Phone: +49 6421 282 1318, Fax: +49 6421 282 4511
distributed for long times. The relaxation of the particle velocities requires dynamical walls where the gas particles exchange energy with wall particles. In Sect. 2 we consider wall particles whose velocities are chosen from a probability distribution. They scatter elastically with the gas particles. We analytically determine necessary conditions for a "physical wall" where the gas particles’ velocity distribution relaxes to a Maxwell distribution. In Sect. 3 we investigate numerically the deterministic time evolution of the gas particles from their elastic scattering against the wall particles which we model as harmonic oscillators. A summary and conclusions, Sect. 6, closes our presentation.

2 Model for classical particles in a box

One of the simplest model systems for the relaxation to thermal equilibrium are ideal classical particles in a box. We consider a large number $N \gg 1$ of non-interacting point-particles $g_i$ of mass $m$ which are fully characterized by their velocities $v_i$ and their positions $x_i$ ($|x_i| \leq a$) in a one-dimensional box with walls at $|x| = a$. Since the particles do not interact with each other we can treat them separately. They move independently between the walls such as swimmers lap in their individual lanes (swimming-lane model).

2.1 Initial conditions for the box particles

At time $t = 0$, we presume that all particles start at position $x = 0$ in the middle of the box. Their starting velocities are distributed symmetrically, i.e., for each particle $g_i$ with velocity $v_i$ there is a particle $g_i$ with velocity $v_i = -v_i$. The probability distribution for the event to find a particle with velocity $v$ is denoted by the positive, normalized function $P_0(v) = P_0(-v) \geq 0$, $\int_{-\infty}^{\infty} dv P_0(v) = 1$. The typical velocity of the particles at $t = 0$, $v_{\text{typ}}$, obeys $v_{\text{typ}}^2 = \langle v^2 \rangle_0 = \int_{-\infty}^{\infty} dv v^2 P_0(v)$. We assume that all moments of the velocity distribution exist, $(v^n)_0 < \infty$.

2.2 Predictions from statistical mechanics for large times

In our very dilute gas, the interaction between the particles and the walls, not among the particles themselves, is responsible for the thermal equilibrium at large times, as it is expressed, e.g., in the ideal gas law,

$$ pV = N k_B T. \tag{1} $$

Here, $p$ is the pressure which the $N$ particles exert onto the walls of the container of volume $V = 2a$; $k_B$ is the Boltzmann constant which permits us to express the energy content of the wall in terms of the familiar temperature $T$ [2].

For our system of classical particles, classical statistical mechanics makes elaborate predictions beyond [1] about the particles’ properties in thermodynamic equilibrium. Let $\Delta N(x,v,t)$ be the number of particles which can be found in the mesoscopic position interval $[x,x+\Delta x]$ ($\Delta x = a/\sqrt{N} \ll a$) with velocities from the mesoscopic interval $[v,v+\Delta v]$ ($\Delta v = v_{\text{typ}}/\sqrt{N} \ll v_{\text{typ}}$) at time $t$. We write

$$ \Delta N(x,v,t) = N n(x,v,t)(\Delta x)(\Delta v). \tag{2} $$

In the thermodynamical limit, $N \to \infty$ so that $(\Delta x)(\Delta v) \to 0$, $n(x,v,t)$ approaches the familiar Boltzmann distribution function $f(x,v,t)$ [3]. From the Boltzmann distribution function we obtain the distribution functions for the particle positions $W(x,t)$ and their velocities $P(v,t)$ as

$$ W(x,t) = \int_{-\infty}^{\infty} dv f(x,v,t) , \quad P(v,t) = \int_{-a}^{a} dx f(x,v,t). \tag{3} $$

At time $t = 0$, we start from

$$ f(x,v,t=0) = \delta(x) P_0(v) \tag{4} $$

so that $W(x,t=0) = \delta(x)$ and $P(v,t=0) = P_0(v)$. Copyright line will be provided by the publisher
For large times, statistical mechanics predicts that the Boltzmann distribution approaches its thermal equilibrium \( f_{eq}(x, v) \),

\[
    f(x, v, t \to \infty) = f_{eq}(x, v) = \frac{1}{2a} \Theta \left( 1 - \frac{|x|}{a} \right) f_M(v) ; \quad f_M(v) = \sqrt{\frac{m}{2\pi k_B T}} \exp \left( -\frac{mv^2}{2k_B T} \right)
\]

where \( \Theta(x) \) is the Heaviside step-function. The particles are equally distributed in the box, \( W_{eq}(x) = W(x, t \to \infty) = (1/2a) \Theta(1 - |x|/a) \), and their velocity distribution is given by Maxwell’s expression, \( P(v, t \to \infty) = P_{eq}(v) = f_M(v) \).

## 3 Relaxation of particle positions

Thus far, we have not yet specified the properties of the walls. We start with hard walls so that the particles are perfectly reflected: Every particle \( g \) with velocity \( v_f \) which is reflected at the right wall \( (v_f > 0 \mapsto v'_f = -v_f) \) has its mirror particle \( g' \) with velocity \( v_f = -v_f \) which is reflected at the left wall \( (v_f \mapsto v'_f = -v_f = v_f) \). Consequently, the velocity distribution of the particles does not change in time, \( P(v, t) = P_0(v) \).

### 3.1 Free Boltzmann equation in the absence of walls

If the walls were absent, all particles start at \( x = 0 \) and propagate freely according to Newton’s first law,

\[
    x_f(t) = vt .
\]

Consequently, the particles at position \( x \) with velocity \( v \) at time \( t \) arrive at position \( x + v t \Delta t \) with velocity \( v \) at time \( t + \Delta t \). This free propagation in phase space implies

\[
    n(x, v, t) = n(x + v t \Delta t, v, t + \Delta t) .
\]

In the thermodynamic limit and for small \( \Delta t \), the Taylor expansion of this equation implies the free Boltzmann equation,

\[
    \frac{\partial f(x, v, t)}{\partial t} + v \frac{\partial f(x, v, t)}{\partial x} = 0 .
\]

Its general solution is \( f(x, v, t) = g(x - vt, v) \). Together with the initial condition \( f(x, v, 0) = \delta(x) P_0(v) \) we find

\[
    f_{\text{free}}(x, v, t) = \delta(x - vt) P_0(v) .
\]

The velocity distribution does not change in time, \( P(v, t) = P_0(v) \). The position distribution broadens in time, \( W(x, t) = P(x/t)/t \). The particles which were initially concentrated at the origin, disperse into a cloud whose density goes to zero as a function of time.

### 3.2 Free Boltzmann equation in the presence of hard walls

In the presence of hard walls, we consider infinite replicas of the box on the whole \( x \)-axis. Box number \( n \) is equivalent to the interval \([na -a, na +a]\) (extended box scheme). In the extended box scheme, the particle propagate freely, see eq. \( \text{[4]} \). In order to determine their true position, we have to fold the extended box scheme back into the interval for \( n = 0 \) (reduced box scheme). Let us consider \( v_f > 0 \). After \( m \) wall reflections we find the particles in the box \( m \). The true particle position is \( x_f(t) = v_f t - 4na = x_{f,\text{free}} - 4na \) for even \( m = 2n \) (particle velocity \( v_f \)) and \( x_f(t) = 2a - (v_f t - 4na) = 2a + 4na - x_{f,\text{free}} \) for odd \( m = 2n + 1 \) (particle velocity \( -v_f \)). Since the initial velocity distribution is symmetric and does not change in time, \( P(v, t) = P_0(v) \), we obtain for the distribution function for all \( v \)

\[
    f(x, v, t) = \Theta \left( 1 - \frac{|x|}{a} \right) \left( \sum_{n=-\infty}^{\infty} f_{\text{free}}(x + 4na, v, t) + \sum_{n=-\infty}^{\infty} f_{\text{free}}(2a + 4na - x, v, t) \right) .
\]
The free Boltzmann distribution is symmetric under the transformation \((-x, -v) \rightarrow (x, v)\). Therefore, we can simplify this expression to

\[
f(x, v, t) = \Theta \left( 1 - \frac{|x|}{a} \right) \sum_{n=-\infty}^{\infty} f_{\text{free}}(x + 2na, v, t) .
\] (11)

We consider the Fourier series of the Boltzmann distribution with respect to the position coordinate and find for the Fourier coefficients \((k = \frac{n\pi}{a}; n: \text{integer})\)

\[
f_k(v, t) = \frac{1}{2a} \int_{-a}^{a} dx f(x, v, t)e^{-ikx} = \frac{1}{2a} \int_{-\infty}^{\infty} dx f_{\text{free}}(x, v, t)e^{-ikx} = \frac{1}{2a} e^{-ikvt} P_0(v) .
\] (12)

The Boltzmann distribution function in the presence of hard walls and the free Boltzmann distribution function have the same Fourier coefficients at \(k = \frac{n\pi}{a}\) so that

\[
f(x, v, t) = \frac{1}{2a} \Theta \left( 1 - \frac{|x|}{a} \right) \sum_{n=-\infty}^{\infty} e^{in\pi(a)(x-vt)} P_0(v) .
\] (13)

With this result, we can calculate the probability distribution for the particle positions. We use the Fourier transformation for the initial velocity distribution,

\[
P_0(v) = \int_{-\infty}^{\infty} \frac{dv}{2\pi} e^{iv\eta} \tilde{P}_0(\eta) , \quad \tilde{P}_0(\eta) = \int_{-\infty}^{\infty} dv e^{-iv\eta} P_0(v)
\] (14)

with \(\tilde{P}_0(\eta) = \tilde{P}_0(-\eta)\) and find

\[
W(x, t) = \frac{1}{2a} \Theta \left( 1 - \frac{|x|}{a} \right) \sum_{n=-\infty}^{\infty} e^{in\pi(a)x} \int_{-\infty}^{\infty} dv e^{-i\pi(a)vt} P_0(v) = \frac{1}{2a} \Theta \left( 1 - \frac{|x|}{a} \right) \sum_{n=-\infty}^{\infty} e^{in\pi(a)\tilde{P}_0(n\pi t/a)} .
\] (15)

For each \(n \neq 0\), the argument of \(\tilde{P}_0(\eta)\) becomes large for \(t \rightarrow \infty\). We demand

\[
\tilde{P}_0(\eta \rightarrow \infty) = 0 .
\] (16)

This implies that the initial velocity distribution cannot contain a macroscopic number of particles with the same velocity. Then, for large times, the sum in (15) reduces to its contribution from \(n = 0\),

\[
W(x, t \rightarrow \infty) = \frac{1}{2a} \Theta \left( 1 - \frac{|x|}{a} \right) .
\] (17)

For long times, the particles become equally distributed in the box with density \(\rho_0 = N/V = N/(2a)\), as expected from thermodynamic considerations.

It is important to note that we know the particle positions and their velocities exactly at every instant in time. Despite this fact, the particle distribution becomes homogeneous for long times and ‘relaxes’ to its equilibrium distribution. For the particle positions this does not come as a surprise because there is no conservation law which prevents them to distribute equally in space. For the velocity distribution, however, momentum and energy conservation guarantee that it is independent in time for hard walls and our symmetric initial distribution. The relaxation of the velocity distribution is more involved, as we discuss in Sec.4.
3.3 Pressure on the hard walls

The reflection of the particles at the right wall implies a momentum transfer $\Delta P$ to it. All the particles with velocity $v > 0$ which reach the wall within the time span $\Delta t$ transfer the momentum $2mv$ [2]. Therefore,

$$\Delta P = N \int_0^\infty dv (2mv) \int_{a-v\Delta t}^a dx n(x, v, t). \quad (18)$$

For small $\Delta t$ and in the thermodynamic limit, we find for the pressure in a one-dimensional box, $p(t) = \lim_{\Delta t \to 0} (\Delta P)/(\Delta t)$, and with $V = 2a$

$$p(t)V = 2N \int_{-\infty}^{\infty} dv \frac{mv^2}{2} (2a)f(a, v, t) = 2N (\mathcal{E} + H(t)), \quad (19)$$

$$\mathcal{E} = \int_{-\infty}^{\infty} dv \frac{mv^2}{2} P_0(v),$$

$$H(t) = \sum_{n=1}^\infty (-1)^n \int_{-\infty}^{\infty} dv (mv^2)e^{-ln\pi vt/a} P_0(v). \quad (20)$$

The time-dependent terms, $H(t)$, vanish for $t \to \infty$ because the Fourier transformed velocity distribution $\tilde{P}_0(\eta)$ and its derivatives vanish for large arguments. We find for $t > 0$

$$H(t) = m \sum_{n=1}^\infty (-1)^n \tilde{P}'_0 \left( \frac{nt\pi}{a} \right), \quad (21)$$

where $\tilde{P}'_0(\eta)$ denotes the second derivative.

The time-independent term provides the ideal-gas law [1] in one dimension [2], $p(t \to \infty)V = 2N \mathcal{E}$ where $\mathcal{E}$ is the average energy of a particle. For the Maxwell distribution, see eq. (5), we find $\mathcal{E} = k_B T/2$ so that $p(t \to \infty)V = N k_B T$, eq. (1), results.

3.4 Examples

As examples, we consider an exponential velocity distribution and a step-like velocity distribution,

$$P_{\text{ex}}(v) = \frac{1}{2v_0} e^{-|v/v_0|}, \quad \tilde{P}_{\text{ex}}(\eta) = \frac{1}{1 + \eta^2 v_0^2}, \quad (22)$$

$$P_{\text{step}}(v) = \frac{1}{2v_0} \Theta \left( 1 - \frac{|v|}{v_0} \right), \quad \tilde{P}_{\text{step}}(\eta) = \frac{\sin(v_0\eta)}{v_0\eta}. \quad (23)$$

The particle density at the wall is obtained from [15]

$$W(a, t) = \frac{1}{2a} \left( 1 + 2 \sum_{n=1}^\infty (-1)^n \tilde{P}_0(n\pi t/a) \right). \quad (24)$$

With the help of Eq. (27.8.6) in Ref. [5] and Mathematica [6] we find for $t > 0$ ($t_{tr} = a/v_0$)

$$2aW_{\text{ex}}(a, t) = 1 + 2 \sum_{n=1}^\infty \frac{(-1)^n}{1 + (\pi nt/t_{tr})^2} = \frac{1}{(t/t_{tr}) \sinh(t_{tr}/t)}, \quad (25)$$

$$2aW_{\text{step}}(a, t) = 1 + 2 \sum_{n=1}^\infty (-1)^n \frac{\sin(\pi nt/t_{tr})}{\pi nt/t_{tr}} = 1 - \frac{s(t/t_{tr})}{t/t_{tr}}. \quad (26)$$

Here, $s(x) = x - 2n$ for $x \in [-1 + 2n, 1 + 2n]$ so that $|s(x)| \leq 1$. The transient time $t_{tr}$ is given by the time a typical particle needs to travel through the system, $t_{tr} = a/v_0$. After this time, the density at
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![Graphs](image)

**Fig. 1** Time evolution of the particle density at the wall, a, and of the pressure, b, for the step-like and exponential velocity distributions. Note that the average kinetic energy differs for the two distributions, \( \bar{E}_{\text{step}}/(mv_0^2) = 1/3 \) and \( \bar{E}_{\text{exp}}/(mv_0^2) = 2 \).

the wall begins to approach its equilibrium value, \( NW(a, t \to \infty) = \rho_0 \). For the exponential distribution, deviations are of order \( (t/t_{tr})^2 \) for large times. For the step-like velocity distribution, we observe saw-tooth oscillations which die out for long times only proportional to \( (t/t_{tr})^3 \). This shows that the particles swap back and forth through the box and reach their homogeneous distribution only fairly slowly.

The same analysis is readily carried out for the pressure. With the help of Eq. (27.8.6) in Ref. [5] and Mathematica [6] we find for \( t > 0 \) (\( t_{tr} = a/v_0 \))

\[
H_{\text{ex}}(t) = 2mv_0^2 \sum_{n=1}^\infty (-1)^n \frac{1 - 3(n\pi t/t_{tr})^2}{[1 + (n\pi t/t_{tr})^2]^3} = \frac{mv_0^2}{2} \left[ -2 + \frac{3 + \cosh(2t_{tr}/t)}{2[(t/t_{tr}) \sinh(t_{tr}/t)]^3} \right], \tag{27}
\]

\[
H_{\text{step}}(t) = \frac{mv_0^2}{2} \left[ s(t/t_{tr}) + \frac{3(s(t/t_{tr})^2 - 1)}{3(t/t_{tr})^2} \right] = \frac{mv_0^2}{2} \left[ \frac{s(t/t_{tr})}{t/t_{tr}} + \frac{3(s(t/t_{tr})^2 - 1)}{3(t/t_{tr})^2} \right]. \tag{28}
\]

For large times, \( t \gg t_{tr} \), we find for the smooth exponential velocity distribution that \( H_{\text{ex}}(t \gg t_{tr}) \sim (t_{tr}/t)^4 \), i.e., the pressure corrections vanish quickly as a function of time. For the step-distribution we observe again a slow decay with saw-tooth oscillations, \( H_{\text{step}}(t \gg t_{tr}) \sim (t/t_{tr})^{-1} \). The density of particles at the wall and the pressure are shown in Fig. [1].

4 Relaxation of particle velocities

In order to relax the energy of the gas particles, we introduce scattering processes in which the gas particles exchange energy with the walls.

4.1 Dynamic wall and scattering events

In order to simplify the analysis, we assume that the walls are perfectly symmetric. Each scattering event which occurs for the gas particle \( g_\ell \) with velocity \( v_\ell \) at the right wall \((x = a)\) has a mirror event for the particle \( g_\ell \) with velocity \( v_\ell = -v_\ell \) at the left wall \((x = -a)\). In this way, our velocity distribution remains symmetric around \( v = 0 \) at all times. In this section we are primarily interested in the relaxation of the velocity distribution of the gas particles. Therefore, we focus on the velocity, not on the position of the gas particles.

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The right wall is made of \( L \gg N \gg 1 \) particles which move freely in the interval \([a, a + A]\) \((a \gg A > 0)\). The wall particles are scattered elastically at the interval boundaries. The boundary at \( x = a \) is transparent for the gas particles. The velocities of the wall particles are taken from a probability distribution \( D(u) = D(-u) \) which obeys the same restrictions as \( P_0(v) \), i.e., all of its moments exist and its Fourier transform, \( \tilde{D}(\eta) \), decays to zero for large values, \( \lim_{\eta \to \infty} \tilde{D}(\eta) = 0 \).

The gas particle \( g_{\ell} (\ell = 1, \ldots N) \) which starts with velocity \( v_{\ell,0} > 0 \) at time \( t = 0 \) undergoes a first scattering event at time \( t_1 > 0 \) with the wall particle \( w_{\ell,1} \) with velocity \( u_{\ell,1} < 0 \). At time \( t_2 > t_1 \) it is scattered off the left wall by the wall particle \( w_{\ell,2} \) whose velocity \( u_{\ell,2} \) is independent of the velocity of the wall particle \( w_{\ell,1} \). The same applies to the subsequent scattering processes: The scattering partners of the gas particles are all different, \( w_{\ell,n} = w_{\ell',n'} \) only if \( \ell = \ell' \) and \( n = n' \). In this way we assure that the wall has no memory: the outcome of a scattering event does not influence the distribution \( D(u) \). This assumption expresses the fact that the wall particles form a ‘bath’ for the gas particles.

Let the wall particles have the mass \( M > m \). Then, a scattering event between a gas particle with velocity \( v \) and a wall particle with velocity \( u \) results in

\[
\begin{align*}
v' &= \beta u - \alpha v , \\
u' &= r \beta v + \alpha u , \\
r &= \frac{m}{M} , \quad \alpha = \frac{1 - r}{1 + r} , \quad \beta = \frac{2}{1 + r} ,
\end{align*}
\]

with \( 0 < r < 1, 0 < \alpha < 1, \) and \( 1 < \beta < 2 \).

4.2 Master equation for the velocity distribution

When we focus on scattering events at the right wall, we must distinguish three cases. We assume that the wall particle and the gas particle meet at the left wall boundary, \( x = a \).

- \( u < \alpha v / \beta \):
  The gas particle is reflected, \( v' = \beta u - \alpha v < 0 \).

- \( \alpha v / \beta \leq u < v \):
  After the first collision, the gas particle penetrates the wall because its velocity is still positive, \( u' > v' > 0 \). The wall particle is reflected at the wall boundary at \( x = a + A \), and collides with the gas particle again. The gas particle then has the velocity

\[
v'' = \gamma v - 2\alpha \beta u < 0 , \quad \gamma = \alpha^2 - r \beta^2 ,
\]

and escapes from the wall region because \( v'' < u'' \).

- \( v \leq u \):
  In this case, the wall particle escapes from the gas particle. The gas particle penetrates the wall and collides with the wall particle which was reflected at the wall boundary at \( x = a + A \). After the collision, the gas particle has the velocity \( v' = -\beta u - \alpha v < 0 \). It cannot be reached by the wall particle again, \( v' < u' \).

If the average kinetic energy of the gas particles and the wall particles is comparable and in the limit \( m/M \to 0 \), the typical wall particle velocities are small compared to the typical gas particle velocities. Then, only the first case is relevant.
In the limit \( \lambda \to \infty \), the master equation (34) has a unique stationary solution. This is a gain-loss equation for the number of particles \( n \).

Therefore, the exponential velocity distribution \( P_n(\tau; v) = e^{\alpha \tau} \lambda^n \), and consider the limit of a large number of scattering events, \( n \gg 1 \), so that \( \Delta \tau \ll \tau \).

In order to elucidate the physical meaning of Eq. (32), we introduce the artificial time \( \tau = n \Delta \tau \) (\( \Delta \tau = 1 \)), and consider the limit of a large number of scattering events, \( n \gg 1 \), so that \( \Delta \tau \ll \tau \). We write

\[
P(n + 1; v) - P(n; v) = \int_{-\infty}^{\infty} dv' \left( A(v, v')P(n; v') - A(v', v)P(n; v) \right).
\]

In the limit \( n \to \infty \), the time \( \tau \) becomes a continuous mesoscopic time scale and we obtain a master equation [3] for the velocity distribution \( P(\tau; v) \),

\[
\frac{\partial P(\tau; v)}{\partial \tau} = \int_{-\infty}^{\infty} dv' \left( A(v, v')P(\tau; v') - A(v', v)P(\tau; v) \right).
\]

This is a gain-loss equation for the number of particles \( N(v) = N P(v) \) with velocity \( v \). As has been shown in the literature [3], the master equation (34) has a unique stationary solution \( P_{\text{stat}}(v) = \lim_{\tau \to \infty} P(\tau; v) \).

In general, the stationary solution of the master equation (34) is not the Maxwell velocity distribution. As an example, we show the result for \( m/M = 1/2 \) for exponential and step-like velocity distributions of the wall particles in Fig. 2.

\[
D_{\text{ex}}(u) = \frac{1}{2u_0} e^{-|u/u_0|}, \quad D_{\text{step}}(u) = \frac{1}{2u_0} \Theta \left( 1 - \frac{|u|}{u_0} \right).
\]

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The stationary velocity distributions depend only on the choice of the velocity distributions for the wall particles, $D(u)$, and not on the initial velocity distribution of the gas particles, $P_0(v)$. The result is independent of the initial conditions. Note that a Gaussian velocity distribution $D(u)$ does not lead to a Maxwell velocity distribution $P(v)$.

The wall in the above example is not a ‘physical’ wall. According to the definition given in van Kampen’s book [3], a physical wall relaxes the gas particles’ velocities to a Maxwell velocity distribution. For a thermal reservoir, its properties must remain essentially unchanged by the interaction with the gas. If a wall particle transferred or received a substantial amount of energy in an individual scattering process it would carry information about the gas particles. Therefore, for a physical wall, we have to demand that in the limit $m/M \to 0$. More specifically, we presume that the typical kinetic energy of a gas particle and of a wall particle are of the same order of magnitude $m v_{typ}^2 \approx M u_{typ}^2$. Then, the typical velocity of a wall particle is small compared to the typical velocity of a gas particle, i.e., $u_{typ}$ is of the order $\sqrt{m/M} v_{typ} \ll v_{typ}$.

In order to perform the limit $m/M \to 0$, we rewrite Eq. (31) in the form

$$ P(v' > 0) = \int_{-\infty}^{\infty} \frac{dx}{\alpha} D(x) P \left( \frac{\beta x + v_0}{\alpha} \right) + \int_{v_0/(\alpha+\beta)}^{\infty} \frac{dx}{\gamma} P \left( \frac{2\beta x - v_0'}{\gamma} \right) + \int_{v_0/(\alpha+\beta)}^{v_0/\beta} \frac{dx}{\gamma} P \left( \frac{2\alpha x - v_0'}{\gamma} \right), \quad (36) $$

where we used $\lim_{m/M \to 0} P(u; v) = P(v)$. Now we are in the position to let $m/M \to 0$ where $\alpha \approx 1 - 2m/M \to 1$, $\beta \approx 2(1 - m/M) \to 2$, $\gamma \approx (1 - 8m/M) \to 1$. $D(x)$ is finite only in a region which is small compared to the typical values for $v'$. Therefore, we may safely extend the first integral over the whole real axis, and we may ignore the contributions from the second and third integral because $D(v') = 0$ for typical values of $v'$. The excluded region, $v' \in [0, (m/M) u_{typ}]$, becomes vanishingly small in the limit $m/M \to 0$.

The resulting integral equation can be simplified by Fourier transformation. We find, see eq. (44),

$$ \tilde{P}(\eta) = \tilde{D}(\beta \eta) \tilde{P}(\alpha \eta) \quad (37) $$

For the normalized, differentiable, and symmetric $\tilde{P}(\eta)$ and $\tilde{D}(\eta)$, the Taylor expansion of this equation gives $(\tilde{D}(0) = 1, \tilde{D}'(0) = 0, \beta = 2, \alpha = 1 - 2m/M)$

$$ \tilde{P}(\eta) = \left( \tilde{P}(\eta) - \frac{2m^2}{M} \tilde{P}'(\eta) \right) + 2\eta^2 \tilde{D}''(0) \tilde{P}(\eta). \quad (38) $$

Here, we made use of the fact that $\tilde{D}(\eta)$ is almost constant in the region where $\tilde{P}(\eta)$ is finite. This reflects our assumption that $D(v)$ is a narrow distribution in comparison to $P(v)$. The resulting differential equation is readily integrated. We use $\tilde{D}''(0) = \int_{-\infty}^{\infty} du D(u)(-iu)^2 \equiv -\langle u^2 \rangle$, and define the wall temperature $T$ via

$$ M/2 \langle u^2 \rangle = \frac{k_B T}{2}, \quad (40) $$

which corresponds to the equipartition theorem in one dimension. Note, however, that in our case $k_B T/2$ simply is an abbreviation for the average kinetic energy of the wall particles. Then, we find from (38)

$$ \tilde{P}(\eta) = e^{-\eta^2 k_B T/(2m)} \quad (41) $$
so that we finally obtain the Maxwell velocity distribution for the gas particles,

\[ P(v) = f_M(v) = \sqrt{\frac{m}{2\pi k_B T}} \exp \left( -\frac{mv^2}{2k_B T} \right). \tag{42} \]

The average kinetic energies of the gas particles and the wall particles are the same, \( M\langle u^2 \rangle = \langle m\langle v^2 \rangle = k_B T \), but their typical velocities differ by a factor \( \sqrt{m/M} \), \( u_{\text{typ}} = \sqrt{\langle u^2 \rangle} = \sqrt{m/M} v_{\text{typ}} \) with \( v_{\text{typ}} = \sqrt{\langle v^2 \rangle} \).

## 5 Numerical simulations for a deterministic system

Finally, we present the results for a numerical simulation of gas particles in a box with a deterministic, physical wall. For simplicity we choose the left wall to be perfectly reflecting.

### 5.1 Oscillator model

We represent the right wall by harmonic oscillators of mass \( M \) with frequency \( \omega_0 \). Each gas particle \( g_i \) \((i = 1, 2, \ldots, N)\) undergoes a sequence of collisions with the wall particles \( w_{\ell,i} \) \((i = 1, 2, \ldots, L_\ell; L_\ell \gg 1)\) whose free motion is given by

\[ x_{\ell,i}(t) = a - A \cos(\omega_0 t + \phi_{\ell,i}) \quad \text{and} \quad u_{\ell,i}(t) = (A \omega_0) \sin(\omega_0 t + \phi_{\ell,i}). \tag{43} \]

The length \( A \) parameterizes the ‘penetration depth’ of the gas particle into the wall. We assume it to be a small fraction of the interatomic distance between the wall’s atoms and, therefore, we work with \( A = 1 \cdot 10^{-12} \text{ m} = 0.01 \text{ Å} \). We choose \( a = 0.2 \text{ m} \) for the diameter of the box, \( a/A = 2 \cdot 10^{11} \). The typical phonon frequencies in a solid are \( \omega_0 = 1.3 \cdot 10^{13} \text{ Hz} \) so that \( u_0 = A \omega_0 = 13 \text{ m/s} \). The phases \( \phi_{\ell,i} \in [0, 2\pi] \) are chosen at random. This reflects the fact that the motion of the wall particles is uncorrelated. We shall comment on the case of equal phases in Sect. 5.2.

For long enough times, we expect that we recover the situation of Sect. 4.3. The velocity distribution of the wall particles is given by \((T_0 = 2\pi/\omega_0)\)

\[ D(u) = \frac{1}{T_0} \int_0^{T_0} dt \delta(u - u_0 \sin(\omega_0 t + \phi)) = \frac{1}{\pi} \frac{1}{\sqrt{u_0^2 - u^2}} \quad \text{for} \quad |u| \leq u_0. \tag{44} \]

The Fourier transformed velocity distribution is given by a Bessel function \( \tilde{D}(\eta) = J_0(u_0 \eta) \) which decays to zero for large arguments, \( \tilde{D}(\eta \gg 1/u_0) \propto 1/\sqrt{\eta u_0} \).

From (40) it follows that the wall temperature is given by \( k_B T = M u_0^2 / 2 \) because \( \langle \langle v^2 \rangle = u_0^2 / 2 \) for the velocity distribution (43). Therefore, at room temperature we find \( M \approx 29 \cdot 10^3 \text{ u} \) (atomic mass unit), i.e., of the order of \( O(10^2) \) atoms in the wall constitute a ‘wall particle’. As our mass ratio we set \( m/M = 10^{-3} \), i.e., the gas particles have the mass \( m = 29 \text{ u} \) (nitrogen molecule, \( \text{N}_2 \)).

We expect that the stationary velocity distribution of our gas particles becomes a Gaussian distribution (43) with variance \( \langle v^2 \rangle = k_B T/m = M/(2m) u_0^2 = 500 u_0^2 \). We thus expect \( v_{\text{typ}} = \sqrt{\langle v^2 \rangle} = 23 u_0 \approx 3 \cdot 10^4 \text{ m/s} \) which agrees with the typical velocity of gas particles in a container at room temperature. The time for a typical particle to perform a closed loop through the box is \( t_{\text{typ}} = 4 a / v_{\text{typ}} \approx 1.3 \cdot 10^{-3} \text{ s} \). A good estimate of the number of scatterings \( C(t) \) which a gas particle has undergone after the time \( t \) is given by \( C(t) = O(t/(10 t_{\text{typ}})) \).

At time \( t = 0 \), we distribute our \( N/2 = 1 \cdot 10^7 \) gas particles equidistantly in the velocity interval \([0, v_0]\), \( P_0(v \geq 0) = \Theta(1 - v/v_0)/(2v_0) \), with \( v_0 = 10 u_0 = 130 \text{ m/s} \). The results for negative velocities are obtained by a reflection at the axis \( v = 0 \). Initially, all gas particles start at \( x = 0 \), \( f(x, v, t_0 = 0) = P_0(v) \delta(x) \).
5.2 Results

5.2.1 Random oscillator phase

In Fig. 3 we show the velocity distributions $P(v > 0, t)$ at times $t_0 = 0$, $t_1 = 0.1 \text{s}$, $t_2 = 1 \text{s}$, $t_3 = 10 \text{s}$, corresponding to a number of $C(t_0) = 0$, $C(t_1) = \mathcal{O}(10^1)$, $C(t_2) = \mathcal{O}(10^2)$, $C(t_3) = \mathcal{O}(10^3)$ wall scatterings. Full lines: Maxwell distribution with $\langle v^2 \rangle = \frac{m}{2} u_0^2$. We see that the velocity distribution continuously transforms from the initial step-distribution to the desired Maxwell distribution. The calculated variance of the essentially stationary distribution at $t = t_3$ is $\sigma^2 = 502 u_0^2$, the expected value is $\langle v^2 \rangle = \frac{500 u_0^2}{2m} \equiv k_B T/m$. Apparently, our oscillator model fulfills the criterion for a physical wall because it leads to a relaxation of the initial velocity distribution to a Gaussian. For very small velocities, we observe minor deviations from the Gaussian shape. This can be attributed to the fact that our ratio $m/M$ is finite so that the condition $|v| > (m/M)u_0$ is violated for very small $|v|$, cf. Sect. 4.3.

We started from other non-singular velocity distributions with $P_0(|v| > v_0) = 0$, and also recovered the Maxwell distribution as stationary state of our simulation. In addition, we verified numerically that the Boltzmann distribution for long times $t$ is given by

$$f(x, v, t \gg t_{tr}) = \frac{1}{2a} \Theta \left( 1 - \frac{|x|}{a} \right) f_M(v) .$$

(45)

As expected from our discussion in Sect. 3, the gas particles are equally distributed in the box, and there is no correlation between their position and their velocity.
5.2.2 Fixed oscillator phases

Finally, we address the issue of whether or not our model can be constrained further. In our simulation results shown in Fig. 3, the phase $\phi_{\ell,i}$ of each wall oscillator is chosen at random. If this phase is fixed, e.g., to $\phi_{\ell,i} = 0$, all oscillators start with the same phase at $t = 0$. When the gas particle $g_{\ell}$ reaches the wall, $v_{\ell,0}t_{\ell,1} = a - A$, the first oscillator has the contact phase $\gamma_{\ell,1} = (t_{\ell,1} \mod T_0) (T_0 = 2\pi/\omega_0)$. After its scattering(s) off the wall particle, the gas particle leaves the wall region at $x_{\ell,1}$ with velocity $-v_{\ell,1} < 0$, is reflected at the left wall, and returns to the right wall boundary at time $t_{\ell,2} = (x_{\ell,1} + 3a - A)/v_{\ell,1}$ with velocity $v_{\ell,1}$. The contact phase of the second oscillator is $\gamma_{\ell,2} = (t_{\ell,2} \mod T_0)$. In general, if $t_{\ell,n}$ is the time at which the gas particle $g_{\ell}$ reaches the boundary of the right wall for the $n$th time $t_{\ell,n} = (x_{\ell,n-1} + 3a - A)/v_{\ell,n-1}$ with velocity $v_{\ell,n-1} > 0$, the contact phase is given by $\gamma_{\ell,n} = (t_{\ell,n} \mod T_0)$. The scattering off the wall can be seen as a dynamical map ($n \geq 1$),

$$\Phi : (v_n, \gamma_n) \mapsto (v_{n+1}, \gamma_{n+1}) \quad (46)$$

for the velocity of the gas particles and their contact phase. The map $\Phi$ belongs to the class of Fermi–Ulam accelerators [7].

![Stationary velocity distribution for the gas particles after a large number of collisions with the dynamic wall. The maximal wall particle velocity is $u_0 = 13$ m/s. The mass ratio between gas and wall particles is $m/M = 10^{-3}$, the size of the box is $a = 100A$, and the particles evolve according to the deterministic map $\Phi$. The largest peak is a fix point of the map, $v_p = v^*_+ (3) = 277$ m/s.](image)

In general, the Fermi–Ulam accelerator map does not lead to a Maxwell distribution for the gas particle velocities. In order to see this, we note that $\Phi$ has stationary points, $(v_{n+1}, \gamma_{n+1}) = (v_n, \gamma_n)$. They follow from the solution of the equations

$$t_{n+1} - t_n = \frac{2(a + x(t_n))}{v_n} = \frac{2\pi R}{\omega_0} \quad (R \geq 1: \text{integer}) \quad (47)$$

where $u(t_n) = A\omega_0 \sin(\omega_0 t_n)$ and $x(t_n) = a - A \cos(\omega_0 t_n)$. One finds for $R > R_{\text{min}} = 2ra/(A\pi) \gg r$ that $v^*_+(R) = u_0[2a/A \pm \sqrt{1 - (2ra/(A\pi R))^2}]/(\pi R)$. Moreover, the map supports stationary loops with two and more elements. As we have tested numerically for $a = 100A$, some of the fix-points and loops are attractive with a large basin of attraction around them (e.g., $R = 3$). Thus, the stationary distribution $P(v)$ depends on the initial distribution $P_0(v)$ and consists of a few peaks only, see Fig. 4. In this simulation, we...
also observed that these peaks belong to small values of \( R \). The stationary solutions for large \( R, R \gg 1 \), do not generate attractive fix-points.

The situation changes drastically for large \( ra/A \), i.e. when we choose \( R_{\text{min}} = \mathcal{O}(ra/A) = 10^6 \). As expected for a Fermi–Ulam accelerator model and confirmed by our numerical investigations, the map \( \Phi \) in (46) is chaotic for \( ra \gg A \); see Refs. [8] for a recent introduction to dynamical systems and chaos. For example, tiny numerical errors make it impossible to retrace the gas particles’ trajectories when we reverse the time evolution after a large number of wall scatterings. This implies that the deterministic map in Eq. (46) is acceptable for the thermalization of the gas particles in our toy model as long as we demand that the box is (mesoscopically) large compared to the penetration depth of the gas particle into the wall, \( ra \gg A \). A more detailed investigation of the map \( \Phi \) is beyond the intentions of this work.

### 6 Summary and conclusions

In this work, we studied non-interacting point particles in a box. Since we assume that the initial conditions factorize in the three spatial dimensions, we restricted ourselves to a one-dimensional setup. As initial condition, all gas particles start in the center of the box with a non-singular velocity distribution. The particle positions ‘thermalize’ after a large number of scatterings at the box walls, i.e., the gas particles become equally distributed in the box. This is due to the fact that there is no conservation law for the position coordinate. The notion of equal spatial distribution is valid on mesoscopic length and velocity scales \( \Delta x = a/\sqrt{N}, \Delta v = v_{\text{typ}}/\sqrt{N} \), which requires a large number of gas particles, \( N \gg 1 \).

The relaxation of the gas particles’ velocity distribution to a Maxwell distribution is more subtle because of energy and momentum conservation. We model our walls as a large collection of independent harmonic oscillators, \( L \gg N \). Each gas particle encounters a harmonic oscillator only once (absence of a wall memory). The Markov property is an essential requirement for finding a stationary velocity distribution for the gas particles. In order to find a Maxwell velocity distribution, we must demand in addition that there is a negligible energy transfer between the gas and the wall particles in each collision; otherwise, a single event could leave a trace of information of the gas particles in the reservoir. The condition of small energy transfers leads to the requirement that the wall particle mass \( M \) is large compared to the gas particle mass \( m \), and that their typical velocity \( v_{\text{typ}} \) is small compared with a typical gas particle velocity \( v_{\text{typ}} \). Their average kinetic energies must be the same, \( M \langle u^2 \rangle = m \langle v^2 \rangle \). Finally, the oscillation amplitude of the wall particles \( A \) must be small compared to the size of the box \( a \) so that the map of the Fermi–Ulam accelerator guarantees a chaotic dynamics. When these ‘thermodynamic’ conditions are fulfilled, the velocity distribution of the gas particles approaches a Maxwell distribution for large times. The evolution of the full system of gas and wall particles is fully deterministic but the result, a Boltzmann distribution for the gas-particle subsystem, is naturally obtained from statistical considerations. The ‘temperature’ of the reservoir is defined by the average kinetic energy of the wall particles, \( M \langle u^2 \rangle = k_B T \).

Apparently, our toy model does not describe the details of the relaxation process properly. For example, the scattering of gas particles at the walls must be described quantum mechanically. As a consequence, not every scattering process is inelastic. In fact, most of them are elastic whereby the probability for an elastic reflection is determined by the Debye–Waller factor. Therefore, the relaxation times could be (much) longer for non-interacting gas particles than given here. On the other hand, the interaction between gas particles and their motion through a three-dimensional vessel reduces the relaxation time drastically because the inter-particle scattering opens paths for the exchange of energy and momentum which are not included in our toy model. In any case, the relaxation time also depends on the shape of the initial velocity distribution. If it is peaked around some velocities, it takes much longer to equilibrate than for the step-like distribution used in our example.

Despite its numerous shortcomings we hope that our work will serve its intended main purpose, namely, to provide a simple case study for beginners in statistical mechanics. Our toy model illustrates that the results of measurements on subsystems of thermodynamically large deterministic systems can equally be obtained from thermodynamic considerations.
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