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A probabilistic model for the equilibration of an ideal gas

Santi Prestipino

Dipartimento di Fisica, INFM and Università degli Studi di Messina, 98166 Messina, Italy

Abstract

I present a generalization of the Ehrenfest urn model that is aimed at simulating the approach to equilibrium in a dilute gas. The present model differs from the original one in two respects: (1) the two boxes have different volumes and are divided into identical cells with either multiple or single occupancy; (2) particles, which carry also a velocity vector, are subjected to random, but elastic, collisions, both mutual and against the container walls. I show, both analytically and numerically, that the number and energy of particles in a given urn evolve eventually to an equilibrium probability density W which, depending on cell occupancy, is binomial or hypergeometric in the particle number and beta-like in the energy. Moreover, the Boltzmann entropy $\ln W$ takes precisely the same form as the thermodynamic entropy of an ideal gas. This exercise can be useful for pedagogical purposes in that it provides, although in an extremely simplified case, a probabilistic justification for the maximum-entropy principle.

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Keywords: Urn models; Boltzmann entropy; Maximum-entropy principle

1. Introduction

The modern intuition of the emergence of the second law of thermodynamics from mechanics is mainly grounded upon the behaviour of stochastic urn models, where "particles" are subjected to a *probabilistic dynamics* that eventually generates a sort of thermodynamic equilibrium [1]. Obviously, this stochastic (Markovian) dynamics is only a caricature of the "real" (Newtonian) dynamics; it is much like an effective dynamics which emerges after averaging over many instances of the complicated short-time motion.

E-mail address: santi.prestipino@unime.it (S. Prestipino).

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In the classical Ehrenfest model, N numbered balls are distributed into two urns; at each step of the process, a ball is extracted at random and moved from the urn where it resides to the other. Eventually, the number of balls in each urn fluctuates around $N/2$, with relative deviations from the mean becoming negligible in the large-N limit. This stochastic process is taken to represent the attainment of particle-number equilibrium in a dilute gas diffusing between two communicating vessels of equal volume.

In order to improve the Ehrenfest model so as to make it more realistic, I consider a generalization where the balls/particles are endowed with both a discrete position and a continuous velocity. To be more specific, we are given two boxes, 1 and 2, and N particles in the boxes. Box 1 (2) is divided into V_1 (V_2) identical cells, with $V = V_1 + V_2$ the total cell number. The occupancy c_α of the αth cell can be either multiple ($c_\alpha = 0, 1, 2, \ldots$) or single ($c_\alpha = 0, 1$), with both possibilities being considered. The velocity of the ath particle is v_a, a three-dimensional vector with components v_{ak} ($k = 1, 2, 3$).

To make things simple, positions and velocities are updated independently and by turns, in such a way that the two dynamics of free motion and collisions will proceed in parallel though staying separate. Hence, the stationary state of each set of variables can be analysed on its own. Along this route, one arrives at a probabilistic foundation of the expression of the ideal-gas entropy in thermodynamics and, concurrently, at a justification (in this case only) of the maximum-entropy principle.

2. Position updates

Let us first suppose that each cell can host whatever number of particles. A position update consists of (i) choosing at random one particle, a_r, and one cell, α_r; and (ii) moving a_r from its original cell into α_r. In terms of the variable n, which counts how many particles are hosted in box 1, this defines a stochastic process of the Markov type, with transition probabilities

$$T(n+1 \leftarrow n) = \frac{(N-n)V_1}{NV}, \quad T(n-1 \leftarrow n) = \frac{nV_2}{NV} . \tag{1}$$

The ensuing master equation admits the *binomial* distribution

$$W(n) = \binom{N}{n} \left(\frac{V_1}{V}\right)^n \left(\frac{V_2}{V}\right)^{N-n} \tag{2}$$

as unique stationary distribution [2]. Since the Markov chain is ergodic (i.e., there is a path connecting every (macro) state n to every other n'), any initial distribution $P(n;0)$ will converge, in the long run, to $W(n)$. In particular, the average n goes eventually into NV_1/V, with relative deviations from the mean of $\mathcal{O}(N^{-1/2})$ [2]. The multiplicity of macrostate n, i.e., the number of complexions (microstates) of N numbered particles in the boxes, such that box 1 contains n particles, is just $W(n) \times V^N$. Assuming $n, N-n = \mathcal{O}(N) \gg 1$, the equilibrium entropy $S(n)$, defined as the logarithm of the multiplicity, is additive over the boxes and extensive with N

$$S(n) \sim -n \ln \frac{n}{V_1} - (N-n) \ln \frac{N-n}{V_2} , \tag{3}$$

being maximum for $n = NV_1/V$. In Eq. (3), we recognize the volume contribution to the ideal-gas entropy.

While all of the above is rather standard, a novel result is obtained when each cell in the boxes can contain at most one particle. Now, at each step in the process, the selected particle a_r is moved into a cell α_r that is chosen at random among the vacant sites. The transition probabilities read (with $V_1, V_2 \geqslant N$):

$$T(n+1 \leftarrow n) = \frac{(N-n)(V_1-n)}{N(V-N)}, \; T(n-1 \leftarrow n) = \frac{n(V_2-N+n)}{N(V-N)} \; , \tag{4}$$

yielding a *hypergeometric* stationary distribution for n [2]

$$W(n) = \binom{V}{N}^{-1} \binom{V_1}{n} \binom{V_2}{N-n} \; . \tag{5}$$

As in the previous case, the average n converges eventually to NV_1/V, with relative deviations of $\mathcal{O}(N^{-1/2})$. The multiplicity of state n, i.e., the number of ways N indistinguishable particles can be arranged in the boxes, in such a way that n particles are placed in box 1, is equal to $W(n) \times \binom{V}{N}$. Assuming $n, N-n, V_1-n, V_2-(N-n) = \mathcal{O}(N) \gg 1$, the equilibrium entropy becomes

$$\begin{aligned} S(n) \sim & -n \ln \frac{n}{V_1} - (V_1 - n) \ln \left(1 - \frac{n}{V_1} \right) \\ & - (N-n) \ln \frac{N-n}{V_2} - (V_2 - N + n) \ln \left(1 - \frac{N-n}{V_2} \right) \; , \end{aligned} \tag{6}$$

being maximum for $n = NV_1/V$. Eq. (6) is nothing but the thermodynamic entropy of two ideal *lattice* gases that can mutually exchange energy and particles.

3. Velocity updates

The collision dynamics of equal-mass particles can be roughly schematized as a succession of *random* binary events which, however, are still required to obey energy and momentum conservation [3]. On the macroscopic side, such collision rules go along with the conservation of total *kinetic* energy and total momentum, thus being appropriate only to a very dilute (gaseous) system of particles. If, moreover, we are willing to drop the momentum constraint, provision should be made also for elastic collisions against the walls of the (cubic) container.

As far as the mutual collisions are concerned, I assume their outcome to be as maximally random as possible. This amounts to update the velocities of the colliding particles as

$$v_a \to v_a' = v_a + \xi \hat{r}; \; v_b \to v_b' = v_b - \xi \hat{r} \; , \tag{7}$$

where $\xi = (v_b - v_a) \cdot \hat{r}$, and $\hat{r}$ is picked up at random out of the hemisphere of unit-length vectors forming an acute angle with $v_b - v_a$. If mutual collisions occur at a rate of p, the master equation for the velocities finally reads

$$\pi(\{v'\}; t+1) = \int \mathrm{d}^{3N} v \, \tau(\{v'\} \leftarrow \{v\}) \pi(\{v\}; t) \; , \tag{8}$$

with $\tau = (1-p)\tau_1 + p\tau_2$ and

$$\tau_1(\{v'\} \leftarrow \{v\}) = \frac{1}{3N}\sum_{a=1}^{N}\sum_{k=1}^{3}\left[\delta(v'_{ak}+v_{ak})\prod_{(b,l)\neq(a,k)}\delta(v'_{bl}-v_{bl})\right],$$

$$\tau_2(\{v'\} \leftarrow \{v\}) = \frac{2}{N(N-1)}\sum_{a<b}\left[\frac{1}{2\pi|v_a-v_b|}\delta^3(v'_a+v'_b-v_a-v_b)\right.$$

$$\left.\times\,\delta(v'^2_a+v'^2_b-v^2_a-v^2_b)\prod_{c\neq a,b}\delta^3(v'_c-v_c)\right]. \tag{9}$$

The following properties can be proved [2]:

- A stationary solution to Eq. (8) is $w(\{v\}) = F(v_1^2+\cdots+v_N^2)$, for any properly normalized function F.
- Upon denoting the one- and two-body velocity distributions at time t as $f_1(v_1;t)$ and $f_2(v_1,v_2;t)$, the following exact equation of evolution holds:

$$f_1(v_1;t+1) = (1-p)\left\{\left(1-\frac{1}{N}\right)f_1(v_1;t)+\frac{1}{3N}[f_1(-v_{1x},v_{1y},v_{1z};t)\right.$$

$$\left.+\,f_1(v_{1x},-v_{1y},v_{1z};t)+f_1(v_{1x},v_{1y},-v_{1z};t)]\right\}$$

$$+p\left\{\left(1-\frac{2}{N}\right)f_1(v_1;t)+\frac{2}{N}\times\frac{1}{2\pi}\int \mathrm{d}^3v_2\right.$$

$$\times\int \mathrm{d}^3\Delta\,\frac{1}{|\Delta|}\delta\left[\Delta^2-\left(\frac{v_1-v_2}{2}\right)^2\right]$$

$$\left.\times\, f_2\left(\frac{v_1+v_2}{2}+\Delta,\frac{v_1+v_2}{2}-\Delta;t\right)\right\}. \tag{10}$$

For any function Φ, the ansatz $f_2^{(\mathrm{eq})}(v_1,v_2) = \Phi(v_1^2+v_2^2)$ gives a stationary solution to Eq. (10). However, in case of an isolated system with total energy U, the only admissible solution to Eq. (8) is the microcanonical density $w(\{v\}) \propto \delta(v_1^2+\cdots+v_N^2-U)$,[1] and the Φ function becomes

$$f_2^{(\mathrm{eq})}(v_1,v_2) = \frac{\Gamma(3N/2)}{\Gamma(3(N-2)/2)}(\pi U)^{-3}\left(1-\frac{v_1^2+v_2^2}{U}\right)^{3(N-2)/2-1}, \tag{11}$$

leading in turn to

$$f_1^{(\mathrm{eq})}(v_1) = \frac{\Gamma(3N/2)}{\Gamma(3(N-1)/2)}(\pi U)^{-3/2}\left(1-\frac{v_1^2}{U}\right)^{3(N-1)/2-1}. \tag{12}$$

The latter is the finite-N Maxwell–Boltzmann (MB) distribution [4]. In the N, $U\to\infty$ limit (with $U/N = \mathcal{O}(1)$), one recovers from Eq. (12) the more familiar

[1] U is meant to express the value of the total kinetic energy in units of $m/2$, m being the particle mass.

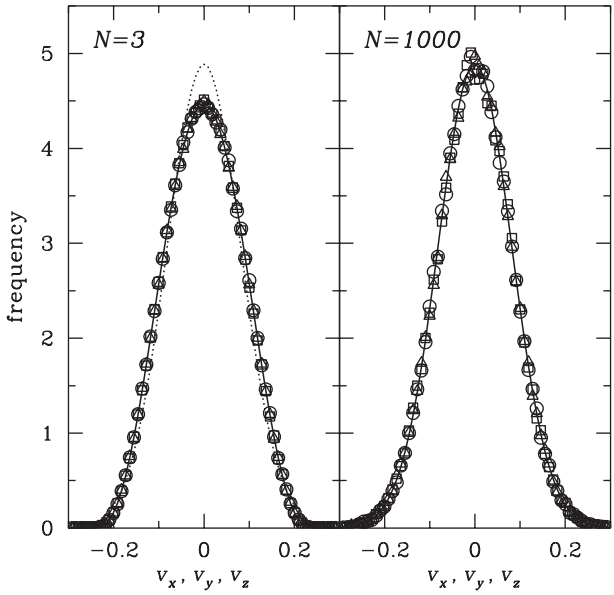

Fig. 1. Numerical simulation of Eq. (8). Hystogram of velocity values for particle 1 (△, □, and ◯ correspond to the x, y, and z component, respectively). Two distinct values of N are compared, i.e., 3 (left) and 1000 (right), while $U/N = 0.02$ in both cases. After rejecting a total of 10^4 collisions per particle (CPP), as many as $\mathcal{N}_{\rm eq}$ CPP are produced ($\mathcal{N}_{\rm eq} = 10^7$ for $N = 3$ and $\mathcal{N}_{\rm eq} = 10^6$ for $N = 1000$). The p value was 0.5, held fixed during the simulation. Data (in form of frequencies of occurrence) are grouped in bins of width $\delta v = 2\sqrt{U/N}/31$ (after equilibration, the hystogram is updated every 10 CPP). The full curve is the theoretical, finite-N MB distribution per velocity component, which, for $N = 3$, is appreciably different from the infinite-N limit (i.e., the Gaussian $\sqrt{\kappa/\pi}\exp(-\kappa v^2)$, with $\kappa = 3N/(2U)$—broken curve in the left panel, full curve in the right panel).

Gaussian form, $f_1^{(\rm eq)}(v) = (\kappa/\pi)^{3/2}\exp(-\kappa v^2)$, with $\kappa = 3N/(2U)$ (corresponding to an average v_a^2 of U/N for all a).

- I have carried out a computer simulation of the evolution encoded in Eq. (8) in order to check whether the stationary distribution (12) is also an asymptotic solution, as expected (at least when $p > 0$) from the ergodicity of kernel (9). First, I set $N = 3$ and $U = 0.06$, with $p = 0.5$. Starting at any particular microstate with energy U, I collect in a hystogram the values, at regular time intervals, of the three components of particle-1 velocity (see Fig. 1 left). Indeed, this hystogram has, in the long run, the finite-N MB form. This is indirect evidence that the simulation trajectory samples uniformly, at least effectively if not literally, the $3N$-dimensional hypersurface of energy U.

  Afterwards, I take $N = 1000$ and $U = 20$, and follow the evolution of the same hystogram as above, now starting from velocity values extracted at random from e.g. a uniform one-particle distribution of variance $U/(3N)$. The long-run distribution of velocity no. 1 compares well with a Gaussian (Fig. 1 right), that is with the large-N form of the MB distribution. In fact, also the instantaneous velocities of all particles

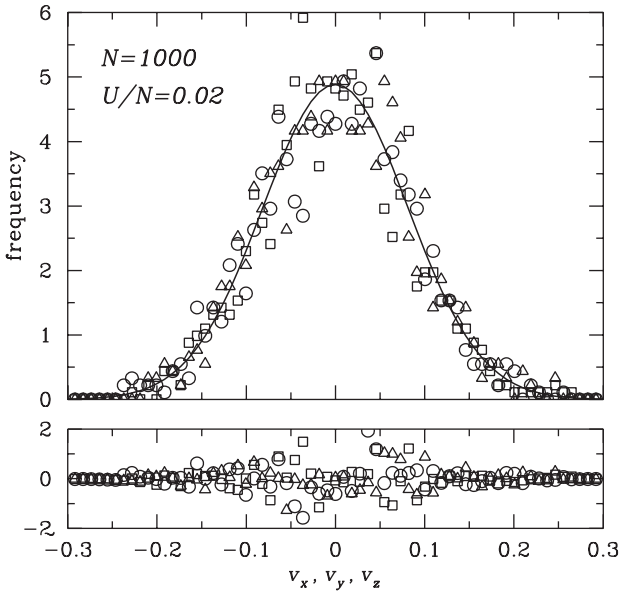

Fig. 2. Numerical simulation of Eq. (8). Top: particle velocities at the end of the simulation run for $N=1000$ and $U=20$ (same symbols and notation as in Fig. 1). The distribution of all-particle velocities at a given time strongly resembles the same Gaussian as in Fig. 1 (full curve). Bottom: difference between the above hystogram and this Gaussian law.

are asymptotically distributed, for large N, according to the same Gaussian (see Fig. 2). This indicates that: (1) the vast majority of points in the energy hypersurface is made of "typical" states, i.e., microstates that look more or less similar as far as low-order distributions like f_1 are concerned; and (2) the microstate at which the evolution was started is, indeed, untypical [5].

- For a given number n of particles in box 1, the equilibrium probability density $W_n(u)$ of their total energy u can be calculated exactly for $w(\{v\}) \propto \delta(v_1^2+\cdots+v_N^2-U)$:

$$W_n(u) = \frac{\Gamma(3N/2)}{\Gamma(3n/2)\,\Gamma(3(N-n)/2)}\, U^{-(3N/2-1)} u^{3n/2-1} (U-u)^{3(N-n)/2-1}\,, \qquad (13)$$

that is, variable u/U is *beta*-distributed with an average of n/N. Of all n-velocity microstates, the fraction of those states whose energy lies between u and $u+\Delta u$ is $W_n(u)\Delta u$ ($\Delta u \ll u$). In particular, the Boltzmann entropy associated with Eq. (13) is, for $n, N-n = \mathcal{O}(N) \gg 1$:

$$\ln W_n(u) \sim -\frac{3n}{2} \ln \frac{n}{u} - \frac{3(N-n)}{2} \ln \frac{N-n}{U-u}\,, \qquad (14)$$

which, when including also the configurational term (3) or (6), gives back the expression of the entropy of the (monoatomic) ideal gas.

In conclusion, I have introduced a stochastic process of the Ehrenfest type which allows one to base the expression of the thermodynamic entropy of an ideal gas on a well-definite microscopic model, without relying on the hypothesis of equal

a priori probability of all microstates. Rather, the validity of the latter, at least in an effective sense, follows as an outcome from the stochastic dynamics itself. In thermodynamics, the second law requires the maximization of the total entropy S under the given constraints (here, the total number of particles N and the total energy U of two ideal gases in grand-canonical contact) in order to find the equilibrium state of an overall isolated system. In the present model, this very same prescription emerges naturally, when defining entropy *à la* Boltzmann, as the condition upon which the partition of N and U between the gases be, in the long-time regime, the most probable.

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