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The ideal gas as an urn model: derivation of the entropy formula

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Abstract

The approach of an ideal gas to equilibrium is simulated through a generalization of the Ehrenfest ball-and-box model. In the present model, the interior of each box is discretized, i.e., balls/particles live in cells whose occupation can be either multiple or single. Moreover, particles occasionally undergo random, but elastic, collisions between each other and against the container walls. I show, both analytically and numerically, that the number and energy of particles in a given box eventually evolve to an equilibrium distribution W which, depending on cell occupations, is binomial or hypergeometric in the particle number and beta-like in the energy. Furthermore, the long-run probability density of particle velocities is Maxwellian, whereas the Boltzmann entropy $\ln W$ exactly reproduces the ideal-gas entropy. Besides its own interest, this exercise is also relevant for pedagogical purposes since it provides, although in a simple case, an explicit probabilistic foundation for the ergodic hypothesis and for the maximum-entropy principle of thermodynamics. For this reason, its discussion can profitably be included in a graduate course on statistical mechanics.

1. Introduction

After the pioneering work of Boltzmann, there is now a general consensus on the idea that dynamically chaotic motion generically leads, in systems of very many particles, to thermodynamic behaviour. A general proof of this statement is however lacking, and one's intuition usually appeals to simplified dynamical models which allow for some analytic treatment. Statistical toy models that illustrate how thermodynamic equilibrium is established in practice are especially helpful for educational scope, since they supply students with a plain justification and a direct understanding of the basic assumptions of thermodynamics and statistical mechanics. In particular, an intuitive picture of the emergence of the second law of thermodynamics from mechanics is provided by the behaviour of stochastic urn

models, where balls/particles are subjected to a *probabilistic* evolution which, eventually, drives the system towards a stationary state [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.

In the Ehrenfest model, N numbered balls are distributed into two urns; at each time step, a number between 1 and N is extracted at random, and the ball with that label is moved from the urn where it resides to the other. Eventually, the average number of balls in each urn becomes equal to $N/2$, with relative fluctuations around the mean that are negligible in the large-N limit. This stochastic process, which Kac considered as 'probably one of the most instructive models in the whole of physics' [2], gives an illustration of the irreversible diffusive dynamics of two dilute gases of the same species, hosted in two communicating, but globally isolated, vessels of equal volume. As we learn from thermodynamics, and is confirmed by experience, the two gases eventually attain an equilibrium state being characterized by an equal number of particles in the two vessels.

In order to also include energetic considerations in the description, I consider a generalization of the Ehrenfest model where the balls/particles are endowed with both a discrete position and a continuous velocity. To be specific, we are given two boxes, 1 and 2, and N labelled particles distributed between the boxes. Box 1 (2) is divided into V_1 (V_2) identical cells, $V = V_1 + V_2$ being the total cell number. The occupation number c_α of the αth cell ($\alpha = 1, \ldots, V$) can be either Bose-like ($c_\alpha = 0, 1, 2, \ldots$) or Fermi-like ($c_\alpha = 0, 1$), with both possibilities being considered in the following. The velocity of the ath particle ($a = 1, \ldots, N$) is $\mathbf{v}_a$, a three-dimensional vector with components v_{ak}, $k = 1, 2, 3$.

To make some progress in the analytic treatment of the model, a drastic simplification is made, namely that the position dynamics is totally decoupled from the velocity dynamics. This is obtained by an independent and alternate updating of positions and velocities, in such a way that free diffusive motion and collisions will run in parallel, yet staying separate. In particular, the equilibrium of one set of variables can be analysed without making reference to the other. The assumption of decoupling between position and velocity updating is tantamount to the hypothesis that (1) the Markov time step, while being much longer than any microscopic collision time, is nevertheless shorter than the time needed for the velocity distribution to relax (i.e., to reach equilibrium); (2) velocity relaxation occurs on a time scale that is also well separated from (typically much longer than) the equilibration time of the number density.

I argue, and indeed it is verified *a posteriori*, that this model gives a representation of the ideal-gas dynamics once defining the entropy with the logarithm of the probability density of macrostate variables. Hence, by this route one arrives at a novel (i.e., not based on the microcanonical ensemble) microscopic foundation of the ideal-gas expression for the entropy and, at the same time, at a probabilistic justification of the maximum-entropy principle of thermodynamics. Furthermore, this simple model gives the opportunity to discuss at length the issue of ergodicity of a probabilistic evolution and its relevance for the actual deterministic dynamics of a many-particle system. This point is usually hardly understood by graduate students in statistical physics, who find it rather obscure. The present model could come in useful for providing an easy access to such basic theoretical questions.

The outline of this paper is the following: in sections 2 and 4, I describe the stochastic dynamics of particle positions and velocities, respectively. Section 3 is an *intermezzo*, mainly of illustrative value, where I show an example of exact derivation of a macro-variable (coarse-grained) evolution from the microscopic dynamics. Further comments and conclusions are given in section 5.

2. Update of positions

Let us first suppose that each cell in the boxes can host whatever number of particles. A position update consists of (1) choosing at random one particle, a_r, and one cell, α_r and (2) moving particle a_r into cell α_r. In terms of the macro-variable n, which counts how many particles are currently found in box 1, this defines a stationary stochastic process of the Markov type, being characterized by the following conditional (or transition) probabilities:

$$\begin{aligned} T(n+1 \leftarrow n) &\equiv P(n+1; t+1|n; t) = \frac{(N-n)V_1}{NV}; \\ T(n-1 \leftarrow n) &\equiv P(n-1; t+1|n; t) = \frac{nV_2}{NV}. \end{aligned} \tag{1}$$

In equation (1), $t = 0, 1, 2, \ldots$ is a discrete time. The ensuing master equation for n reads

$$\begin{aligned} P(n; t+1) = &\frac{(N-n+1)V_1}{NV} P(n-1; t) + \frac{(n+1)V_2}{NV} P(n+1; t) \\ &+ \left(1 - \frac{(N-n)V_1}{NV} - \frac{nV_2}{NV}\right) P(n; t). \end{aligned} \tag{2}$$

It can immediately be realized, by direct inspection, that equation (2) admits the *binomial* distribution

$$W(n) = \binom{N}{n} \left(\frac{V_1}{V}\right)^n \left(\frac{V_2}{V}\right)^{N-n} \tag{3}$$

as unique stationary distribution. 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 $W(n)$. Observe that $W(n)$ gives the chance that, upon randomly distributing N labelled particles into two boxes, with different *a priori* probabilities for the boxes, the number of particles in box 1 will be n. Moreover, the multiplicity of macrostate n, i.e., the number of complexions (microstates) of N distinguishable particles in the boxes, such that box 1 contains n particles, is $V^N W(n)$. Hereafter, I list a number of properties which hold for the dynamics ruled by equation (2).

First, I calculate the average n and n^2 at any time by explicitly evaluating the two sums

$$\begin{aligned} \langle n \rangle(t+1) &\equiv \sum_{n=0}^{N} n P(n; t+1) = \frac{V_1}{V} + \left(1 - \frac{1}{N}\right) \langle n \rangle(t); \\ \langle n^2 \rangle(t+1) &\equiv \sum_{n=0}^{N} n^2 P(n; t+1) \\ &= \frac{V_1}{V} + \left(1 - \frac{2}{N}\right) \langle n^2 \rangle(t) + \left[\left(1 - \frac{1}{N}\right) \frac{2V_1}{V} + \frac{1}{N}\right] \langle n \rangle(t). \end{aligned} \tag{4}$$

The first of the difference equations (4) admits a solution $\langle n \rangle(t) = a + bx^t$, for suitable a, b and x. One easily finds

$$\langle n \rangle(t) = \frac{NV_1}{V} + \left(\langle n \rangle(0) - \frac{NV_1}{V}\right) \left(1 - \frac{1}{N}\right)^t, \tag{5}$$

i.e., an irreversible exponential approach to NV_1/V, a value corresponding to having the same density of particles in every box. Similarly, the second of equations (4) has a solution of the form

$$\langle n^2 \rangle(t) = a' + b' \left(1 - \frac{1}{N}\right)^t + c' \left(1 - \frac{2}{N}\right)^t, \tag{6}$$

with $a' = NV_1/V + N(N-1)(V_1/V)^2$. Whence the variance of n scales, in the infinite-time limit, as N:

$$\frac{\sqrt{\langle n^2\rangle - \langle n\rangle^2}}{\langle n\rangle} \to \frac{1}{\sqrt{N}}\sqrt{\frac{V_2}{V_1}}. \tag{7}$$

Assuming $n, N-n, V_1, V_2 = \mathcal{O}(N) \gg 1$ and using the Stirling approximation $\ln N! = N(\ln N - 1) + \mathcal{O}(\ln N)$, the equilibrium entropy $S(n)$, defined as the logarithm of the multiplicity $V^N W(n)$, turns out to be additive over the boxes and extensive with n:

$$S(n) \sim -n \ln \frac{n}{V_1} - (N-n)\ln\frac{N-n}{V_2} + N\ln N, \tag{8}$$

being maximum for $n = NV_1/V$ (subextensive terms in (8) are ignored). Note that the superextensive $N\ln N$ term turns into an extensive constant if $V^N W(n)$ is multiplied by the Gibbs factor of $1/N!$, whose origin is quantum-mechanical (it arises as a required correction to the partition function of a system of identical particles in the classical limit, i.e., under the hypothesis of low particle density at *all* temperatures). In equation (8), we recognize the volume contribution to the ideal-gas entropy. Therefore, the equilibrium (and asymptotic) value of n is the outcome of the entropy maximization, as indeed prescribed by thermodynamics.

It easily follows from equation (3) that the profile of $W(n)$ around the maximum is Gaussian,

$$\ln W(n) = \text{const} - \frac{V^2\Delta n^2}{2NV_1V_2} + \mathcal{O}\left(\frac{\Delta n^3}{N^2}\right), \tag{9}$$

$\Delta n = n - NV_1/V$ being the deviation from the abscissa of the maximum. The last term in equation (9) is negligible for standard deviations $\Delta n = \mathcal{O}(\sqrt{N})$.

Nothing changes in the asymptotics if α_r is forbidden to be the same original cell of a_r. In this case,

$$T(n+1 \leftarrow n) = \frac{(N-n)V_1}{N(V-1)}; \qquad T(n-1 \leftarrow n) = \frac{nV_2}{N(V-1)}, \tag{10}$$

but the form of $W(n)$ is unchanged. However,

$$\langle n\rangle(t) = \frac{NV_1}{V} + \left(\langle n\rangle(0) - \frac{NV_1}{V}\right)\left(1 - \frac{V}{N(V-1)}\right)^t \tag{11}$$

is slightly different from (5), though sharing the same limit NV_1/V for $t \to \infty$.

While all of the above sounds quite 'standard', novel results are those I obtain for the case of single-occupation cells. Now, at each step of 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 now read (with $V_1, V_2 \geqslant N$):

$$T(n+1 \leftarrow n) = \frac{(N-n)(V_1-n)}{N(V-N)}; \qquad T(n-1 \leftarrow n) = \frac{n(V_2-N+n)}{N(V-N)}, \tag{12}$$

yielding a *hypergeometric* stationary distribution for variable n:

$$W(n) = \binom{V}{N}^{-1}\binom{V_1}{n}\binom{V_2}{N-n}. \tag{13}$$

The Vandermonde identity,

$$\sum_{n=0}^{N}\binom{V_1}{n}\binom{V_2}{N-n} = \binom{V_1+V_2}{N}, \tag{14}$$

ensures that equation (13) is normalized correctly. $W(n)$ gives the chance that, upon randomly choosing N cells (i.e., the occupied ones) among a total of V distinguishable sites, the number of particles in box 1 is n. Stated differently, $\binom{N}{n}$ is the number of ways n numbered particles can be sorted out from a set of N, while

$$\frac{V_1}{V}\frac{V_1-1}{V-1}\cdots\frac{V_1-(n-1)}{V-(n-1)}\frac{V_2}{V-n}\frac{V_2-1}{V-(n+1)}\cdots\frac{V_2-(N-n-1)}{V-(N-1)} \tag{15}$$

is the number of ways *these* n particles can be allocated in box 1 (the other $N-n$ being attributed to box 2 instead). The product of $\binom{N}{n}$ by (15) gives again $W(n)$. Finally, the multiplicity of state n, i.e., the number of ways N indistinguishable particles can be arranged into V distinguishable cells, in such a way that n particles reside in box 1, is equal to $\binom{V_1}{n}\binom{V_2}{N-n} = \binom{V}{N}W(n)$.

The average n and n^2 at time t are given by

$$\begin{aligned}\langle n\rangle(t) &= \frac{NV_1}{V} + \left(\langle n\rangle(0) - \frac{NV_1}{V}\right)\left(1-\frac{V}{N(V-N)}\right)^t;\\ \langle n^2\rangle(t) &= a' + b'\left(1-\frac{V}{N(V-N)}\right)^t + c'\left(1-\frac{2(V-1)}{N(V-N)}\right)^t,\end{aligned} \tag{16}$$

with $a' = [NV_1V_2+N^2V_1(V_1-1)]/[V(V-1)]$. In the infinite-time limit, the relative deviation from the average

$$\frac{\sqrt{\langle n^2\rangle - \langle n\rangle^2}}{\langle n\rangle} \to \frac{1}{\sqrt{N}}\sqrt{\frac{V_2(V-N)}{V_1(V-1)}}. \tag{17}$$

Upon assuming $n, N-n, V_1-n, V_2-N+n = \mathcal{O}(N) \gg 1$, the equilibrium entropy becomes

$$\begin{aligned}S(n) \equiv \ln\left[\binom{V_1}{n}\binom{V_2}{N-n}\right] \sim & -n\ln\frac{n}{V_1} - (V_1-n)\ln\left(1-\frac{n}{V_1}\right)\\ & -(N-n)\ln\frac{N-n}{V_2} - (V_2-N+n)\ln\left(1-\frac{N-n}{V_2}\right),\end{aligned} \tag{18}$$

being maximum for $n = NV_1/V$. Equation (18) is nothing but the thermodynamic entropy of two ideal *lattice* gases that can mutually exchange energy and particles.

Finally, it immediately follows from equation (13) that the profile of $W(n)$ around the maximum is Gaussian,

$$\ln W(n) = \text{const} - \frac{V^3\Delta n^2}{2N(V-N)V_1V_2} + \mathcal{O}\left(\frac{\Delta n^3}{N^2}\right) + \mathcal{O}\left(\frac{\Delta n^3}{(V-N)^2}\right), \tag{19}$$

$\Delta n = n - NV_1/V$ being the deviation from the abscissa of the maximum. Again, the last two terms in equation (19) are negligible for standard deviations $\Delta n = \mathcal{O}(\sqrt{N})$.

3. Derivation of a coarse-grained dynamics from the microstate dynamics

For a specific instance of stochastic dynamics of cell occupation numbers, I provide in this section the detailed derivation of the coarse-grained evolution of a macro-variable (i.e., the number n of occupied cells in box 1).

In the example considered here, the occupation numbers $c_\alpha = 0, 1$ are made to evolve according to the following rules: at each time step (1) two cells are chosen at random (either in the same box or in different boxes) and (2) their occupation numbers are mutually—and unconditionally—exchanged (observe that the overall number N of occupied cells is conserved

by the dynamics). The ensuing Monte Carlo/Markovian evolution is thus specified by the transition probabilities

$$\tau(\{c'\} \leftarrow \{c\}) = \frac{2}{V(V-1)} \sum_{\alpha<\beta} \left(\delta_{c'_\alpha, c_\beta} \delta_{c'_\beta, c_\alpha} \prod_{\gamma \neq \alpha, \beta} \delta_{c'_\gamma, c_\gamma} \right), \tag{20}$$

where the constant prefactor in (20) ensures the correct normalization, namely that

$$\sum_{\{c'\}} \tau(\{c'\} \leftarrow \{c\}) = 1. \tag{21}$$

Taking $\pi(\{c\}; t)$ to be the probability for the occurrence of the microstate $\{c\}$ at time t, the master equation of micro-evolution formally reads

$$\pi(\{c'\}; t+1) = \sum_{\{c\}} \tau(\{c'\} \leftarrow \{c\}) \pi(\{c\}; t). \tag{22}$$

Upon plugging equation (20) into equation (22), the latter equation becomes

$$\pi(\ldots, c_\alpha, \ldots, c_\beta, \ldots; t+1) = \frac{2}{V(V-1)} \sum_{\alpha<\beta} \pi(\ldots, c_\beta, \ldots, c_\alpha, \ldots; t), \tag{23}$$

which admits the constant $\binom{V}{N}^{-1}$ as a stationary solution.

Let the V cells be numbered in such a way that the first V_1 cells in the list belong to box 1, while those from $V_1 + 1$ to V belong to box 2. The probability of observing the macrostate n at time t is then

$$P(n; t) = \sum_{\{c\}} \delta_{\sum_{\gamma=1}^{V_1} c_\gamma, n} \pi(\{c\}; t). \tag{24}$$

I aim at finding an equation of evolution for this P, namely a master equation that is valid at a less fundamental, coarse-grained level of description.

First, I note that every sum over all distinct pairs of cells (like that appearing on the rhs of equation (23)) can be decomposed into three sums, $\sum_{\alpha<\beta\leqslant V_1} + \sum_{\alpha\leqslant V_1<\beta} + \sum_{V_1<\alpha<\beta}$, the three partial sums being denoted as A, B and C, respectively. Also observe that, for $\alpha < \beta \leqslant V_1$ or $V_1 < \alpha < \beta$, the value of n is left unchanged by the exchange of c_α and c_β, and the same happens for $\alpha \leqslant V_1 < \beta$ provided $c_\alpha = c_\beta$. Conversely, for $\alpha \leqslant V_1 < \beta$, n increases (or decreases) by 1 when $c_\alpha = 0$ and $c_\beta = 1$ (or the other way around).

Let S_n be the set of all the $\binom{V_1}{n}\binom{V_2}{N-n}$ microstates $\{c\}$ such that $\sum_{\gamma=1}^{V_1} c_\gamma = n$. Upon summing the lhs of equation (23) over S_n, the net result is, by definition, $P(n; t+1)$. Similarly, summing A and C over the same microstates gives

$$\frac{V_1(V_1-1)}{2} P(n; t) \qquad \text{and} \qquad \frac{V_2(V_2-1)}{2} P(n; t), \tag{25}$$

respectively. As to the pairs $\alpha < \beta$ contributing to B, i.e., satisfying $\alpha \leqslant V_1 < \beta$, the microstates of S_n are classified in four categories, according to the values of c_α and c_β. Calling $\mathcal{N}_{\alpha,\beta}$ the total number of pairs of each type, one has

$$\begin{aligned}
&c_\alpha = c_\beta = 1: && \mathcal{N}^{(1)}_{\alpha,\beta} = n(N-n);\\
&c_\alpha = c_\beta = 0: && \mathcal{N}^{(2)}_{\alpha,\beta} = (V_1-n)(V_2-N+n);\\
&c_\alpha = 1 \quad \text{and} \quad c_\beta = 0: && \mathcal{N}^{(3)}_{\alpha,\beta} = n(V_2-N+n);\\
&c_\alpha = 0 \quad \text{and} \quad c_\beta = 1: && \mathcal{N}^{(4)}_{\alpha,\beta} = (V_1-n)(N-n).
\end{aligned} \tag{26}$$

In particular, the coefficient of $P(n;t)$ in the master equation for n should be

$$\frac{2}{V(V-1)}\left(\frac{V_1(V_1-1)}{2}+\frac{V_2(V_2-1)}{2}+n(N-n)+(V_1-n)(V_2-N+n)\right)$$
$$=1-\frac{2(V_1-n)(N-n)+2n(V_2-N+n)}{V(V-1)}. \tag{27}$$

Now observe that, for each microstate of S_n, there are exactly $\mathcal{N}^{(3)}_{\alpha,\beta}$ terms in the sum $\sum_{\alpha\leqslant V_1<\beta}\pi(\ldots,c_\beta,\ldots,c_\alpha,\ldots;t)$ that refer to microstates of S_{n-1}. Hence, the coefficient of $P(n-1;t)$ in the master equation (i.e., the number of times any specific microstate of S_{n-1} is repeated in the sum $\sum_{\{c\}\in S_n}\sum_{\alpha\leqslant V_1<\beta}\pi(\ldots,c_\beta,\ldots,c_\alpha,\ldots;t)$) is given by the product of $\mathcal{N}^{(3)}_{\alpha,\beta}$ times the number of S_n microstates, divided by the total number of S_{n-1} microstates:

$$\frac{n(V_2-N+n)\binom{V_1}{n}\binom{V_2}{N-n}}{\binom{V_1}{n-1}\binom{V_2}{N-n+1}}=(V_1-n+1)(N-n+1), \tag{28}$$

which is also the number of S_n microstates that can be originated from any specific microstate of S_{n-1} by moving a particle from box 2 to 1.

A similar calculation for the coefficient of $P(n+1;t)$ yields

$$\frac{(V_1-n)(N-n)\binom{V_1}{n}\binom{V_2}{N-n}}{\binom{V_1}{n+1}\binom{V_2}{N-n-1}}=(n+1)(V_2-N+n+1). \tag{29}$$

In the end, the complete master equation for n reads

$$P(n;t+1)=\frac{2(V_1-n+1)(N-n+1)}{V(V-1)}P(n-1;t)+\frac{2(n+1)(V_2-N+n+1)}{V(V-1)}P(n+1;t)$$
$$+\left(1-\frac{2(V_1-n)(N-n)+2n(V_2-N+n)}{V(V-1)}\right)P(n;t). \tag{30}$$

One can easily extract from the above equation the expression for the transition probabilities, with the result

$$T(n+1\leftarrow n)=\frac{2(V_1-n)(N-n)}{V(V-1)};\qquad T(n-1\leftarrow n)=\frac{2n(V_2-N+n)}{V(V-1)}. \tag{31}$$

The latter probabilities, although not identical to (12), nonetheless lead to the same stationary distribution (13), as can be checked directly. This is not strange, since the transition probabilities (31) are obtained by multiplying (12) for the constant factor $2N(V-N)/[V(V-1)]$.

4. Update of velocities

The collision dynamics of a set of equal-mass particles can be schematized, at the roughest level of description, as a succession of *random* binary events which are nevertheless 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 want to drop the momentum constraint, provision should be made also for elastic collisions of particles against the (cubic) container walls, causing the reversal of one component only of the velocity of the hitting particle (say, the x component if the collision occurs against the wall that is orthogonal to the x axis).

As far as the mutual collisions are concerned, the conservation laws by themselves require that the velocities of the colliding particles, say a and b, be updated as

$$\mathbf{v}_a \to \mathbf{v}'_a = \mathbf{v}_a + (\Delta v)\hat{\mathbf{r}}; \qquad \mathbf{v}_b \to \mathbf{v}'_b = \mathbf{v}_b - (\Delta v)\hat{\mathbf{r}}, \tag{32}$$

where $\Delta v = (\mathbf{v}_b - \mathbf{v}_a)\cdot\hat{\mathbf{r}}$, and all that we know about the unit-length vector $\hat{\mathbf{r}}$ is that it forms an acute angle with $\mathbf{v}_b - \mathbf{v}_a$ (i.e., $\Delta v > 0$). In particular, note that a general property of an elastic collision is

$$|\mathbf{v}'_a - \mathbf{v}'_b| = |\mathbf{v}_a - \mathbf{v}_b|. \tag{33}$$

The full specification of $\hat{\mathbf{r}}$ would require more knowledge about the collision (i.e., the peculiar geometry of the impact and the exact law of interaction between the particles). Instead, the collision rules considered here are such that the outcome of a mutual collision is *as maximally random as possible*: that is, at each step of the game, $\hat{\mathbf{r}}$ is picked up at random from the hemisphere of unit vectors forming an acute angle with $\mathbf{v}_b - \mathbf{v}_a$.[1] Note that only in one dimension is the vector $\hat{\mathbf{r}}$ nonetheless univocally determined: this is consistent with the known fact that, for particles moving on a straight line and colliding elastically, the conservation laws suffice to determine the post-collision velocities from the initial ones. I point out that the duration of velocity relaxation in a real system is rather sensitive to the peculiarities of the interaction between particles. However, this may not be the case for the asymptotic shape of the velocity distribution, which is only aware of the conservation laws that rule the outcome of an individual collision.

If collisions against walls and between particles occur at a rate of $1-p$ and p, respectively (where p is any number between 0 and 1), the master equation for the velocities reads

$$\pi(\{\mathbf{v}'\}; t+1) = \int \mathrm{d}^{3N} v\, \tau(\{\mathbf{v}'\} \leftarrow \{\mathbf{v}\})\pi(\{\mathbf{v}\}; t), \tag{34}$$

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

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

$$\tau_2(\{\mathbf{v}'\} \leftarrow \{\mathbf{v}\}) = \frac{2}{N(N-1)}\sum_{a<b}\left[\frac{1}{2\pi|\mathbf{v}_a - \mathbf{v}_b|}\delta^3(\mathbf{v}'_a + \mathbf{v}'_b - \mathbf{v}_a - \mathbf{v}_b)\right. \tag{35}$$

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

Note that the two kernels τ_1 and τ_2 are separately normalized. In particular, the factor $1/(2\pi|\mathbf{v}_a - \mathbf{v}_b|)$ is the outcome of a six-dimensional integration of delta functions, which is performed by substituting $\mathbf{v}'_a$ and $\mathbf{v}'_b$ with the auxiliary variables $\mathbf{s} = (\mathbf{v}'_a + \mathbf{v}'_b)/2$ and $\mathbf{t} = (\mathbf{v}'_a - \mathbf{v}'_b)/2$ (the Jacobian for this transformation is 8):

$$\int \mathrm{d}^3 v'_a\, \mathrm{d}^3 v'_b\, \delta^3(\mathbf{v}'_a + \mathbf{v}'_b - \mathbf{v}_a - \mathbf{v}_b)\delta\big(v'^2_a + v'^2_b - v^2_a - v^2_b\big)$$

$$= 8\int \mathrm{d}^3 s\, \mathrm{d}^3 t\, \delta^3[2\mathbf{s} - (\mathbf{v}_a + \mathbf{v}_b)]\delta\big[2(s^2 + t^2) - \big(v^2_a + v^2_b\big)\big]$$

[1] In order to sample uniformly the three-dimensional spherical surface of unit radius, it is necessary to extract (θ, ϕ) pairs distributed according to $\frac{1}{2\pi}\times\frac{1}{2}\sin(\theta)$. In a computer, this is accomplished through the usual generator of pseudo-random numbers: call R_θ a variate that is uniformly distributed between 0 and 1, $\Theta = \arccos(1 - 2R_\theta)$ is then distributed according to $\frac{1}{2}\sin(\theta)$.

$$= 8\pi \int_0^{+\infty} \mathrm{d}t\, t^2 \delta\left[t^2 - \left(\frac{\mathbf{v}_a - \mathbf{v}_b}{2}\right)^2\right]$$
$$= 2\pi |\mathbf{v}_a - \mathbf{v}_b|. \tag{36}$$

Using equations (33) and (36), it is easy to prove that a stationary solution to equation (34) is, for any regular and properly normalized function F,

$$w(\{\mathbf{v}\}) = F\left(v_1^2 + \cdots + v_N^2\right). \tag{37}$$

An outstanding exception is $p = 1$, where the more general stationary solution to equation (34) is instead $F\left(v_1^2 + \cdots + v_N^2\right) G(\mathbf{v}_1 + \cdots + \mathbf{v}_N)$, for arbitrary F and G functions.

Next, I consider the one- and two-body velocity distributions at time t. These are marginal distributions that are built over $\pi(\{\mathbf{v}\}; t)$:

$$\begin{aligned} f_1(\mathbf{v}_1; t) &= \int \mathrm{d}^3 v_2\, \mathrm{d}^3 v_3 \cdots \mathrm{d}^3 v_N\, \pi(\{\mathbf{v}\}; t); \\ f_2(\mathbf{v}_1, \mathbf{v}_2; t) &= \int \mathrm{d}^3 v_3 \cdots \mathrm{d}^3 v_N\, \pi(\{\mathbf{v}\}; t). \end{aligned} \tag{38}$$

Seeking for an exact equation of evolution for f_1, I calculate $f_1(\mathbf{v}_1; t+1)$ by inserting equation (34) into the first of equations (38). While the term arising from τ_1 can be easily worked out, less straightforward is the derivation of the other one, involving τ_2:

$$\int \mathrm{d}^3 v_2 \cdots \mathrm{d}^3 v_N \int \mathrm{d}^{3N} v'\, \tau_2(\{\mathbf{v}\} \leftarrow \{\mathbf{v}'\}) \pi(\{\mathbf{v}'\}; t)$$
$$= \left(1 - \frac{2}{N}\right) f_1(\mathbf{v}_1; t) + \frac{2}{N(N-1)} \sum_{b>1} \int \mathrm{d}^{3N} v' \frac{1}{2\pi |\mathbf{v}'_1 - \mathbf{v}'_b|} \pi(\{\mathbf{v}'\}; t)$$
$$\times \int \mathrm{d}^3 v_b\, \delta^3(\mathbf{v}_1 + \mathbf{v}_b - \mathbf{v}'_1 - \mathbf{v}'_b) \delta\left(v_1^2 + v_b^2 - v_1'^2 - v_b'^2\right), \tag{39}$$

where the latter sum is actually made of $N-1$ identical contributions. Then, considerations similar to those leading to equation (36) allow one to further simplify the rhs of equation (39) and to arrive at the final equation for f_1, whose status is akin to that of the famous Boltzmann equation in the kinetic theory of gases:

$$f_1(\mathbf{v}_1; t+1) = (1-p) \left\{ \left(1 - \frac{1}{N}\right) f_1(\mathbf{v}_1; t) + \frac{1}{3N} [f_1(-v_{1x}, v_{1y}, v_{1z}; t) \right.$$
$$\left. + f_1(v_{1x}, -v_{1y}, v_{1z}; t) + f_1(v_{1x}, v_{1y}, -v_{1z}; t)] \right\}$$
$$+ p \left\{ \left(1 - \frac{2}{N}\right) f_1(\mathbf{v}_1; t) + \frac{2}{N} \times \frac{1}{2\pi} \int \mathrm{d}^3 v_2 \int \mathrm{d}^3 \Delta\, \frac{1}{\Delta} \delta\left[\Delta^2 - \left(\frac{\mathbf{v}_1 - \mathbf{v}_2}{2}\right)^2\right] \right.$$
$$\left. \times f_2\left(\frac{\mathbf{v}_1 + \mathbf{v}_2}{2} + \Delta, \frac{\mathbf{v}_1 + \mathbf{v}_2}{2} - \Delta; t\right) \right\}. \tag{40}$$

While it seems problematic to derive a sort of H-theorem from equation (40), an easier program to fulfil is to find time-independent solutions for this equation. It can immediately be checked that the ansatz $f_2^{(\mathrm{eq})}(\mathbf{v}_1, \mathbf{v}_2) = \Phi\left(v_1^2 + v_2^2\right)$ gives a stationary solution to equation (40) for any appropriate function Φ (for $p = 1$, the more general time-independent solution is instead

$\Phi\big(v_1^2+v_2^2\big)\Psi(\mathbf{v}_1+\mathbf{v}_2)$). However, in the case of an isolated system with total energy U,[2] the only admissible solution (37) is the microcanonical density

$$w(\{\mathbf{v}\}) = \frac{\Gamma(3N/2)}{\pi^{3N/2}} U^{-(\frac{3N}{2}-1)} \delta\big(v_1^2+\cdots+v_N^2-U\big). \tag{41}$$

In this case, the Φ function can be explicitly worked out by transforming to hyperspherical coordinates:

$$\begin{aligned} f_2^{(\mathrm{eq})}(\mathbf{v}_1,\mathbf{v}_2) &= \frac{\int \mathrm{d}^3v_3\cdots\mathrm{d}^3v_N\,\delta\big(U-v_1^2-v_2^2-\sum_{a=3}^N v_a^2\big)}{\int \mathrm{d}^3v_1\cdots\mathrm{d}^3v_N\,\delta\big(U-\sum_{a=1}^N v_a^2\big)} \\ &= \frac{S_{3(N-2)}(1)\int_0^{+\infty}\mathrm{d}r\, r^{3(N-2)-1}\delta\big[r^2-\big(U-v_1^2-v_2^2\big)\big]}{S_{3N}(1)\int_0^{+\infty}\mathrm{d}r\, r^{3N-1}\delta(r^2-U)} \\ &= \frac{\Gamma(3N/2)}{\Gamma(3(N-2)/2)}(\pi U)^{-3}\left(1-\frac{v_1^2+v_2^2}{U}\right)^{\frac{3(N-2)}{2}-1}, \end{aligned} \tag{42}$$

$S_n(R)=2\pi^{n/2}R^{n-1}/\,\Gamma(n/2)$ being the area of the n-dimensional hyperspherical surface of radius R. A similar calculation leads to

$$f_1^{(\mathrm{eq})}(\mathbf{v}_1) = \frac{\Gamma(3N/2)}{\Gamma(3(N-1)/2)}(\pi U)^{-\frac{3}{2}}\left(1-\frac{v_1^2}{U}\right)^{\frac{3(N-1)}{2}-1}, \tag{43}$$

which 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 equation (43) the more familiar Gaussian form

$$f_1^{(\mathrm{eq})}(\mathbf{v}) = \left(\frac{\kappa}{\pi}\right)^{\frac{3}{2}} \mathrm{e}^{-\kappa v^2}, \tag{44}$$

with $\kappa = 3N/(2U)$, corresponding to an average v_a^2 of U/N for all a. Note that full independence of $\mathbf{v}_1$ and $\mathbf{v}_2$, namely $f_2^{(\mathrm{eq})}(\mathbf{v}_1,\mathbf{v}_2)=f_1^{(\mathrm{eq})}(\mathbf{v}_1)f_1^{(\mathrm{eq})}(\mathbf{v}_2)$, requires the thermodynamic limit $N\to\infty$ and $U=\mathcal{O}(N)$.

As a further comment, I emphasize that a distribution like (37) is a meaningful solution to equation (34) also for F not being a delta function. In fact, the $t=0$ velocity distribution need not necessarily correspond to a single microstate or to a mixture of microstates all having the same energy U. It is an equally valid possibility that the initial state encompasses a whole distribution of microstate energies. In this case, and taking for granted that the evolution is ergodic, the collisions will eventually suppress any difference in weight between the microstates having the same energy, but preserving the overall frequency of occurrence of every energy value in the mixture.

A normalized w distribution of the form (37) requires that F satisfies

$$\int_0^{+\infty}\mathrm{d}U\,F(U)U^{\frac{3N}{2}-1} = \frac{\Gamma(3N/2)}{\pi^{3N/2}}. \tag{45}$$

Upon observing that

$$F\big(v_1^2+\cdots+v_N^2\big) = \int_0^{+\infty}\mathrm{d}U\,F(U)\delta\big(v_1^2+\cdots+v_N^2-U\big), \tag{46}$$

the two- and one-body velocity distributions will read

$$\begin{aligned} f_2^{(\mathrm{eq})}(\mathbf{v}_1,\mathbf{v}_2) &= \frac{\pi^{\frac{3(N-2)}{2}}}{\Gamma(3(N-2)/2)}\int_{v_1^2+v_2^2}^{+\infty}\mathrm{d}U\,F(U)\big(U-v_1^2-v_2^2\big)^{\frac{3(N-2)}{2}-1}; \\ f_1^{(\mathrm{eq})}(\mathbf{v}_1) &= \frac{\pi^{\frac{3(N-1)}{2}}}{\Gamma(3(N-1)/2)}\int_{v_1^2}^{+\infty}\mathrm{d}U\,F(U)\big(U-v_1^2\big)^{\frac{3(N-1)}{2}-1}. \end{aligned} \tag{47}$$

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

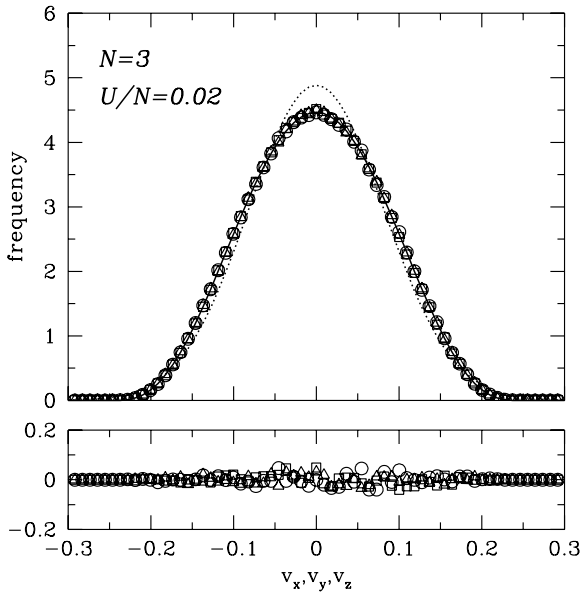

Figure 1. Numerical simulation of equation (34). Top: histogram of velocity values for particle 1 (△, □ and ○ correspond to the x, y, and z components, respectively). Here, $N = 3$ and $U = 0.06$. After rejecting a total of 10^5 collisions per particle (CPP) (so as to sweep away any memory of the initial state), as many as 10^7 CPP are produced. The p value is 0.5, held fixed during the simulation. Data (in the form of frequencies of occurrence) are grouped in bins of width $\delta v = 2\sqrt{U/N}/31$. After equilibration, the histogram is updated every 10 CPP. The full curve is the theoretical, finite-N MB distribution per single velocity component, which 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). Bottom: here is plotted the difference between the histogram and the finite-N MB distribution.

The above distributions do not generally have a Gaussian profile, even in the thermodynamic limit (an exception is $F(U) = \pi^{-3N/2}\exp(-U)$, which leads to $f_1^{(\mathrm{eq})}(\mathbf{v}_1) = \pi^{-3/2}\exp(-v_1^2)$ and $f_1^{(\mathrm{eq})}(\mathbf{v}_1, \mathbf{v}_2) = \pi^{-3}\exp(-v_1^2 - v_2^2)$).

I have carried out a computer simulation of the evolution encoded in equation (34) in order to check whether the stationary distribution (43) is also an asymptotic, $t \to \infty$ solution to equation (34), as one may surmise (at least for $0 < p < 1$) from the likely ergodic character of its kernel τ. First, I set $N = 3$ and $U = 0.06$, with $p = 0.5$ (note that the choice of U is rather immaterial, it just sets the range of fluctuations of a single velocity component to approximately a value of $2\sqrt{U/(3N)}$). Starting from a system of velocities in any particular microstate of energy U, I collect in a histogram the values, at regular time intervals, of the three components of, say, the velocity of particle 1. A look at figure 1 indeed shows that this histogram 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. I note that ergodicity does not hold for $p = 0$ (i.e., when only collisions against the walls are present), whereas the stochastic evolution for $p = 1$ (i.e., only mutual collisions present) retains memory of the initial value of the total momentum.

Afterwards, I take $N = 1000$ and $U = 20$ (i.e., the same U/N as in the previous case), and follow the evolution of the same histogram as above, now starting from velocity values that are randomly extracted from, e.g., a (bounded) *uniform* one-particle distribution of zero average and variance equal to $U/(3N)$ (I have checked that nothing changes in the results

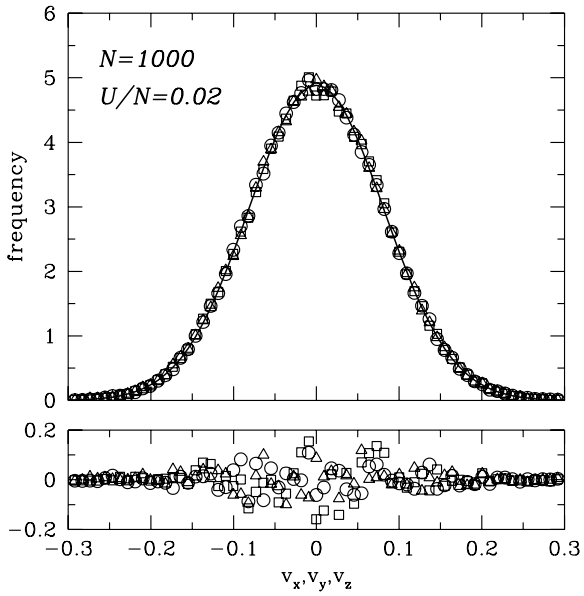

Figure 2. Numerical simulation of equation (34). Top: histogram of velocity values for particle 1 (same symbols and notation as in figure 1). Now, $N = 1000$ and $U = 20$ (i.e., same U/N as in figure 1). Initially, the v_a vectors are extracted from a uniform one-particle distribution having zero average and a variance of $U/(3N)$ (hence the maximum speed $v_{\max} = \sqrt{U/N}$). Then, velocities are rescaled to fit the chosen U value. After discarding 10^4 CPP, a huge number of collisions is performed (10^6 per particle, with $p = 0.5$). Similarly to $N = 3$, data are grouped in bins of width $\delta v = 2v_{\max}/31$ and the histogram is updated every 10 CPP. The full curve is the theoretical distribution, that is the Gaussian $\sqrt{\kappa/\pi}\,\exp(-\kappa v^2)$, with $\kappa = 3N/(2U)$. Bottom: difference between the histogram and the above Gaussian.

if the shape of the initial one-velocity distribution were different, e.g., truncated quadratic). After discarding the initial part of the simulation trajectory, the long-run distribution of values for velocity no 1 now compares well with a Gaussian (see figure 2), that is with the large-N form of the MB distribution. In fact, also the instantaneous velocities of all particles are asymptotically distributed, for large N, according to the same Gaussian (see figure 3). 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, marginal distributions like f_1 are concerned, (2) the microstate at which the evolution (34) was started is actually untypical and (3) this evolution eventually moves the initial state into the manifold of typical microstates. It is believed that such features of the stochastic dynamics (34) and (35) are owned also by the deterministic dynamics of a typical many-particle system. In particular, it is in the weak or effective sense being clarified in point (3) above that the ergodic hypothesis of statistical mechanics may actually be relevant for mechanical systems (and are the most) that are not strictly ergodic [5][3].

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 $w(\{\mathbf{v}\}) \propto \delta\left(v_1^2 + \cdots + v_N^2 - U\right)$, by evaluating the probability that the number $v_1^2 + \cdots + v_n^2$ be comprised in an interval (a, b), with $a > 0$.

[3] See these points more extensively discussed in the first part of [5], as well as in the contributing paper by Goldstein in the second part of [5].

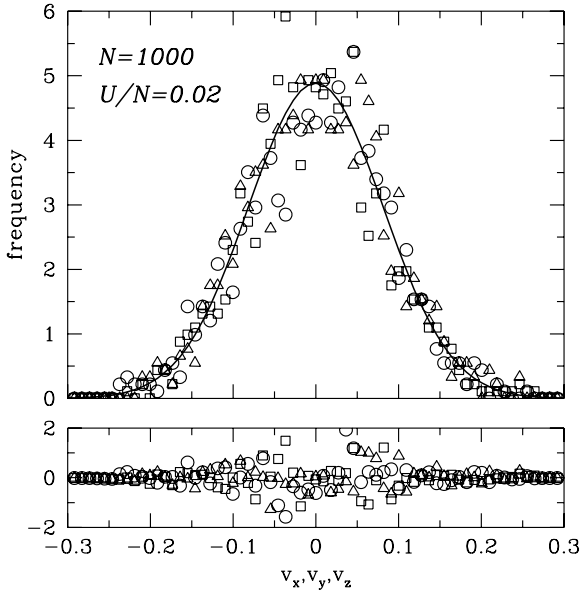

Figure 3. Numerical simulation of equation (34). Top: particle velocities at the end of the simulation run for $N = 1000$ and $U = 20$ (see figure 2, caption; same symbols and notation as in figure 1). The distribution of all-particle velocities at a given time strongly resembles the same Gaussian as in figure 2 (full curve). Bottom: difference between the above histogram and this Gaussian law (note the change of scale with respect to figures 1 and 2).

Once again, this probability is calculated by transforming to hyperspherical coordinates:

$$P\left(v_1^2+\cdots+v_n^2\in(a,b)\right)=\frac{S_{3n}(1)S_{3(N-n)}(1)\int_{\sqrt{a}}^{\sqrt{b}}\mathrm{d}r\,r^{3n-1}\int_0^{+\infty}\mathrm{d}\rho\,\rho^{3(N-n)-1}\delta(\rho^2+r^2-U)}{S_{3N}(1)\int_0^{+\infty}\mathrm{d}r\,r^{3N-1}\delta(r^2-U)}$$

$$=\frac{\Gamma(3N/2)}{\Gamma(3n/2)\Gamma(3(N-n)/2)}U^{-(\frac{3N}{2}-1)}\int_a^b\mathrm{d}u\,u^{\frac{3n}{2}-1}(U-u)^{\frac{3(N-n)}{2}-1}. \tag{48}$$

Hence, the final result

$$W_n(u)=\frac{\Gamma(3N/2)}{\Gamma(3n/2)\Gamma(3(N-n)/2)}U^{-(\frac{3N}{2}-1)}u^{\frac{3n}{2}-1}(U-u)^{\frac{3(N-n)}{2}-1}, \tag{49}$$

that is, the variable u/U is *beta* distributed with an average of n/N and a variance of $(n/N)(1-n/N)/(3N/2+1)$ (which is $\mathcal{O}(N^{-1})$ for $n=\mathcal{O}(N)$). Of all n-velocity microstates, the fraction of those states whose energy lies between u and $u+\Delta u$ is $W_n(u)\Delta u$ (for $\Delta u \ll u$). In particular, the Boltzmann entropy associated with equation (49) is, for $n, N-n=\mathcal{O}(N)\gg 1$:

$$\ln W_n(u)\sim-\frac{3n}{2}\ln\frac{n}{u}-\frac{3(N-n)}{2}\ln\frac{N-n}{U-u}+\frac{3N}{2}\ln\frac{N}{U}, \tag{50}$$

which, when including also the configurational term (8) or (18), gives back the correct expression of the entropy of the (monoatomic) ideal gas:

$$\frac{S}{k_B}=N\ln\frac{V}{N}+\frac{3N}{2}\ln\frac{U}{N}. \tag{51}$$

5. Conclusions

Simple, yet non-trivial, theoretical models hold a prominent place in our own understanding of physical reality, since they help in corroborating in our mind the general abstract principles. This is especially true for the learning of statistical mechanics, where the appeal of students to their physical intuition, which is grounded on every-day experience, is not as easy as for classical mechanics and therefore the convinced acceptance of basic principles by them would require a proper mediation.

An example is the hypothesis of equal *a priori* probability of all microstates, which is crucial for getting at the microcanonical and canonical ensembles. In this paper, I have introduced a stochastic process of the Ehrenfest type which, among other things, provides a microscopic justification for the expression of the thermodynamic entropy of an ideal gas, i.e., without relying on any ergodic hypothesis. Rather, the validity of this hypothesis, at least in an effective sense, arises automatically from the stochastic dynamics itself. However, in order to make the asymptotics of the present model solvable a rather strong assumption was made, i.e., that positions and velocities actually behave as uncorrelated random variables. This is only justified so long as the two sets of variables relax on very different time scales, which is a fair assumption only for low-density gases (i.e., for particles undergoing only sporadic encounters). The proposed derivation of the ideal-gas entropy somehow recalls the heuristic estimate of the multiplicity by [6, 7], though being definitely more rigorous.

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 being in grand-canonical contact with each other) in order to find the equilibrium state of an overall isolated system. In the present model, this very same prescription emerges naturally, when defining the entropy in the same style as Boltzmann, as the condition upon which the partition of N and U between the gases is, in the long-time regime, the (overwhelming for $U, N \gg 1$) most probable. Hopefully, a discussion of this model with the students can serve to deepen their comprehension of the hypotheses underlying statistical mechanics.

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