

Ehrenfest urn revisited: Playing the game on a realistic fluid model

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The Ehrenfest urn process, also known as the dogs and fleas model, is realistically simulated by molecular dynamics of the Lennard-Jones fluid. The key variable is Δz —i.e., the absolute value of the difference between the number of particles in one half of the simulation box and in the other half. This is a pure-jump stochastic process induced, under coarse graining, by the deterministic time evolution of the atomic coordinates. We discuss the Markov hypothesis by analyzing the statistical properties of the jumps and the waiting times between the jumps. In the limit of a vanishing integration time step, the distribution of waiting times becomes closer to an exponential and, therefore, the continuous-time jump stochastic process is Markovian. The random variable Δz behaves as a Markov chain and, in the gas phase, the observed transition probabilities follow the predictions of the Ehrenfest theory.

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I. INTRODUCTION

A fundamental question in statistical mechanics is the reconciliation of the irreversibility of thermodynamics with the reversibility of the microscopic equations of motion governed by classical mechanics. In 1872 Boltzmann gave an answer with his *H* theorem [1], describing the increase in the entropy of an ideal gas as an irreversible process. However, the proof of this theorem contained the *Stoßzahlansatz*—i.e., the assumption of molecular chaos. The result was subject to two main objections: Loschmidt’s *Umkehrwand* (reversibility paradox) [2,3] and Zermelo’s *Wiederkehrwand* (recurrence paradox) [4]. Boltzmann’s reply to the two objections was not fully understood at the time, but is now considered as a cornerstone of statistical mechanics. It is summarized in the article that Ehrenfest and Ehrenfest wrote for the German *Encyclopedia of Mathematical Sciences* [5]. Subsequently, Boltzmann’s approach has been reformulated in the language of stochastic processes [6–8].

Essentially, even in the presence of a deterministic microscopic dynamics, the *coarse graining* of configuration space due to the observer’s state of knowledge results in a stochastic process where the number of particles in a given cell varies at random as a function of time.

Exactly 100 years ago [9], Ehrenfest and Ehrenfest gave a simple and convincing interpretation of Boltzmann’s ideas in term of an urn stochastic process that is a periodic Markov chain in their original formulation [5,10,11]. There are N marbles or balls to be divided into two equal parts of a box. In order to fix the ideas, let us call P the number of balls in the left part and Q the number of balls in the right part. The balls are labeled from 1 to N . At each step of the process, an

integer between 1 and N is selected with probability $1/N$ and the corresponding ball is moved from one part to the other. Rather than urns and balls, later variants of the model used dogs and fleas jumping from one dog to the other, but this does not change the mathematics. Indeed, according to Ref. [11], Ehrenfest and Ehrenfest already had something similar to fleas in mind because they used the verb *hüpfen*, meaning *hop*, which is more appropriate for fleas than for marbles. Assuming $P > Q$, in terms of the random variable $\Delta z = |P - Q|$, the unconditional equilibrium probability of a certain value of Δz is given by

$$p_{\text{eq}}(\Delta z) = \binom{N}{P} \left(\frac{1}{2}\right)^N = \binom{N}{(N + \Delta z)/2} \left(\frac{1}{2}\right)^N. \quad (1)$$

In the limit for $N \rightarrow \infty$ [6],

$$p_{\text{eq}}(\Delta z) \sim \sqrt{\frac{2}{N\pi}} \exp\left(-\frac{(\Delta z)^2}{2N}\right). \quad (2)$$

The transition probabilities of a decrease, $p_d(\Delta z - 2|\Delta z)$, and of an increase, $p_u(\Delta z + 2|\Delta z)$, of Δz are given by

$$p_d(\Delta z - 2|\Delta z) = \frac{P}{N} = \frac{N + \Delta z}{2N}, \quad (3a)$$

$$p_u(\Delta z + 2|\Delta z) = \frac{Q}{N} = \frac{N - \Delta z}{2N}. \quad (3b)$$

Equations (3) completely determine the Ehrenfest-urn Markov chain. It is possible to define an aperiodic version of this process, but both versions share the same stationary distribution (invariant measure) given by Eq. (1), which in the aperiodic case is also the equilibrium distribution [10,12]. As noticed by Kohlrausch and Schrödinger [13,14], Eq. (1) can be regarded as the equilibrium distribution for a fictitious walker obeying a suitable forward Kolmogorov equation,

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$$p(P, t+1) = \frac{P+1}{N} p(P+1, t) + \frac{N-P+1}{N} p(P-1, t). \quad (4)$$

By means of this stochastic process, Ehrenfest and Ehrenfest were able to present convincing evidence in favor of Boltzmann's approach. In this example, the random variable Δz is analogous to H and it almost always decreases from any higher value; moreover, this is true in both the direct and reverse time directions as required by Loschmidt's *Umkehr-einwand* and Δz is quasiperiodic as required by Zermelo's *Wiederkehr-einwand* [5].

But what happens if this game is played with a real fluid or, more modestly, with a realistic model [15,16] of a fluid? As argued by Boltzmann, in this case the deterministic microscopic dynamics induces a stochastic process and, again, the number of fluid particles in the left side of the box P and in the right side of the box Q fluctuate as a function of time. Here, the coarse graining is simply due to the division into two equal parts of the box that contains the fluid. The Markov hypothesis, clearly explained by Penrose [8], is instrumental in deriving the properties of statistical equilibrium. There is, however, a further complication. P , Q , and Δz can be constant for a certain time before changing their values. The waiting times between these jumps are randomly distributed as well. The mathematical model for such a process is called a *continuous-time pure-jump stochastic process* [10]. A pure-jump process is Markovian if and only if the waiting time between two consecutive jumps is exponentially distributed (this distribution may depend on the initial nonabsorbing state) [10]. The following remark is important. It is possible to define a pure-jump process by coupling a Markov chain, such as the Ehrenfest-urn process defined above, with a point process for the interjump waiting times. If the latter is nonexponential, the pure-jump process is non-Markovian.

In the present work, we investigate the Markovian character of the pure-jump process induced by the simulation of a Lennard-Jones fluid in a box.

II. METHODOLOGY

Systems with $N=500$, 1000, 2000, and 100 000 atoms interacting with the cut and shifted Lennard-Jones pair potential

$$U = \sum_{i<j} [U_{ij}(r_{ij}) - U_{ij}(r_{\text{cut}})],$$

$$U_{ij}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (5)$$

where r_{ij} is the interatomic distance, were simulated using classical molecular dynamics [17,18]. We employed a parallelepiped unit box with side ratios 1:1:1 when $N=1000$ or 2:1:1 in the other cases and periodic boundary conditions in all three directions of space. For $N=1000$, we used also two parallel soft walls in the x direction with periodic boundary conditions in the y, z directions only—i.e., “slab” boundary conditions. The wall potential was given by integrating the Lennard-Jones potential over a semi-infinite wall of atoms distributed with a density ρ_w [19]:

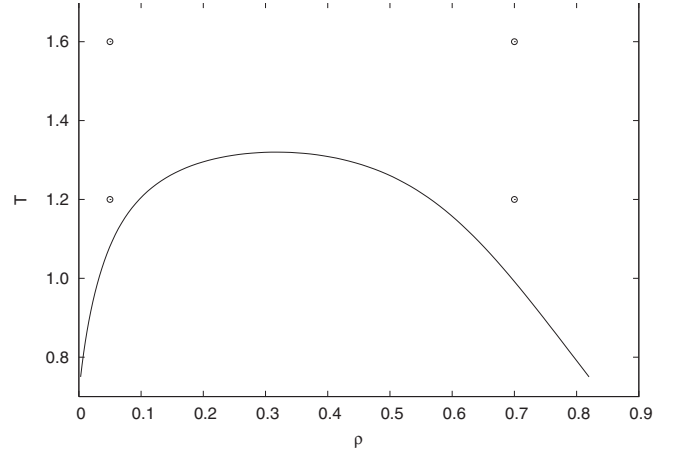


FIG. 1. The four simulated points (circles) in the phase diagram of the Lennard-Jones fluid. The liquid-vapor curve (solid line) is a Bezier fit to data from Ref. [21]. The critical point corresponds to the maximum of the liquid-vapor curve.

$$U_w = \sum_i [U_{iw}(r_{iw}) - U_{iw}(r_{\text{cut}}^w)],$$

$$U_{iw}(r_{iw}) = 4\pi\rho_w\sigma^3\epsilon \left[\frac{1}{45} \left(\frac{\sigma}{r_{iw}} \right)^9 - \frac{1}{6} \left(\frac{\sigma}{r_{iw}} \right)^3 \right], \quad (6)$$

where r_{iw} is the atom-wall distance. We did not put walls along all three directions of space to avoid too large surface effects with small values of N . We use reduced units with $\sigma = \epsilon = m = k_B = 1$, where m is the mass of each atom and k_B is the Boltzmann constant. This defines the time unit as $\sigma\sqrt{m/\epsilon}$ and the temperature unit as ϵ/k_B . We used the common bulk cutoff value $r_{\text{cut}} = 2.7$ and a wall cutoff $r_{\text{cut}}^w = \sqrt[6]{2/5}$ corresponding to the minimum of the wall potential, so that the cut and shifted wall potential is purely repulsive. ρ_w was set to 1—i.e., slightly below the densities of bcc (1.06) and fcc (1.09) lattices. We chose four points in the phase diagram with $(\rho, T) = (0.05, 1.2), (0.7, 1.2), (0.05, 1.6), (0.7, 1.6)$ lying around the critical point, whose accepted value for the Lennard-Jones fluid is (0.35, 1.35) [20,21]; see Fig. 1.

Production runs of 10^7 time steps were done in the micro-canonic ensemble with the velocity Verlet integrator [22,23], while equilibration runs were performed in the canonic ensemble with an extended-system thermostat [23–26]. At every time step we measured P as the number of atoms on the left part of the box—that is, with $r_x < 0$. Thus, as mentioned before, one has $\Delta z = |P - Q| = |2P - N|$; see Fig. 2. While a time step $\Delta t = 0.025$ is sufficient for an acceptable energy conservation in this kind of system [26], to get a good resolution of the waiting times we started employing a smaller $\Delta t = 0.001$; for $N=1000$, we obtained $\sigma_E/|E|$ in the range from 7.0×10^{-6} to 1.1×10^{-4} depending on ρ and T . Nevertheless, any time step we tried down to 0.0001 was still large enough to observe a few percent of jumps in Δz greater than 2; the shorter the average waiting time, the higher the percentage. There were even occasional variations greater than 4 or, for some parameter combinations, 6, 8, or 10.

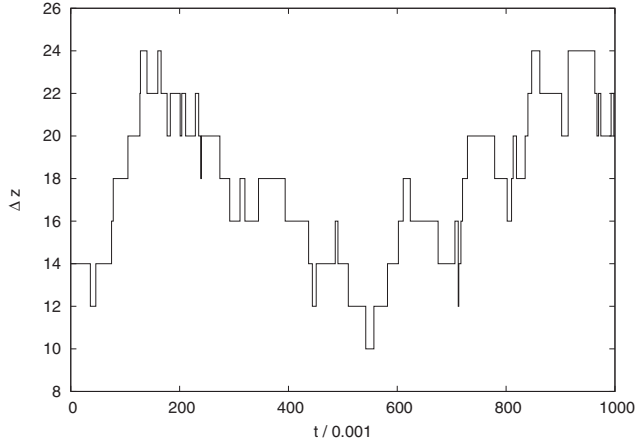


FIG. 2. The pure-jump stochastic process $\Delta z = |P - Q|$ as a function of the first 1000 time steps of the first simulation run in Table I.

A trajectory of 10^7 time steps with $N=1000$ took about 20 h at $\rho=0.05$ and about 80 h at $\rho=0.7$ on a 2.4-GHz Intel Pentium IV processor with our own C++ code using Verlet neighbor lists. With $N=100\,000$, the lower density lasted 17.5 h on 64 IBM Power4+ processors at 1.7 GHz and the higher density almost 9 days on 64 AMD Opteron 270 processors at 2.0 GHz, with a FORTRAN code using domain decomposition and linked-cell lists [27]. Trajectories of this length are the main difference with respect to the pioneering simulations of 40 years ago, when for $N=864$ atoms and $\rho \approx 0.8$ one time step took 45 s on a CDC-3600 [15], while trajectories consisted typically of 1200 time steps [16].

III. RESULTS

A. Analysis of jumps

In this section, we study the random variable Δz . We compare simulation results with the Ehrenfest theory to see whether Δz obeys the Markov-chain equations (1)–(4).

In Fig. 3, the empirical estimate for $p_{eq}(\Delta z)$ is plotted and

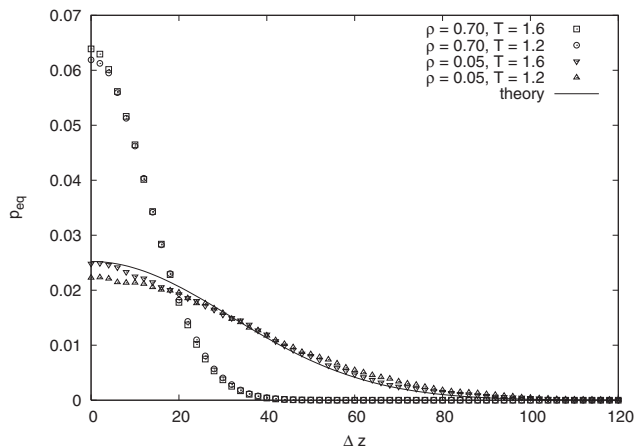


FIG. 3. Histograms of the values of Δz from the runs of the $N=1000$ systems without walls. The theoretical line given by Eq. (2) matches the gas states.

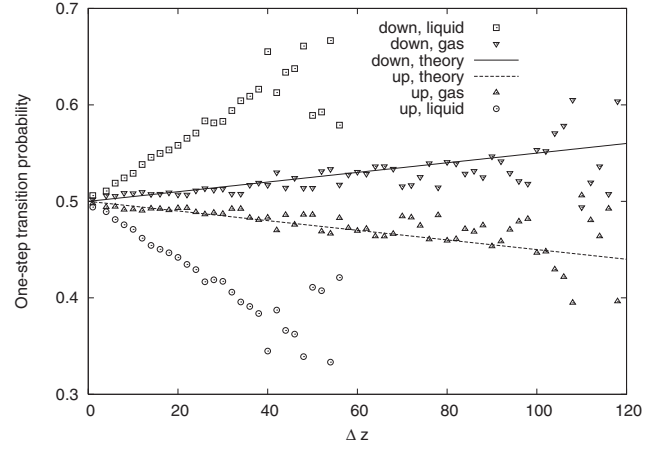


FIG. 4. One-step transition probabilities $p_d(\Delta z - 2|\Delta z)$ and $p_u(\Delta z + 2|\Delta z)$ for $\rho=0.7$, $T=1.2$ (liquid) and $\rho=0.05$, $T=1.6$ (gas), $N=1000$ without walls. The theoretical lines $1/2 \pm \Delta z/(2N)$ [6] match the gas state.

compared with Eq. (2). There is visibly a good agreement between the quantitative prediction of Eq. (2) and the empirical histogram for the gas phase, and this agreement is slightly better for the higher temperature.

In Fig. 4, we report results on the one-step transition probabilities. The Ehrenfest prediction is given by Eqs. (3). Again, in the gas phase of the Lennard-Jones fluid there is agreement between the sampled transition probabilities and the Ehrenfest theory. Even if linear in Δz , the sampled transition probabilities for the liquid phase deviate from Eqs. (3).

Sampled two-step transition probabilities are plotted in Fig. 5. If the process is a Markov chain, these probabilities must be the product of two one-step transition probabilities. This property appears satisfied both for the gas and for the liquid. Moreover, for the gas, the sampled two-step probabilities follow the Ehrenfest quantitative prediction given by Eqs. (3).

Even if, rigorously speaking, we have not shown that, for all n , the n -step transition probabilities are the product of n one-step transition probabilities (see Ref. [28] for processes obeying the semigroup property that are not Markov chains), at least we can claim that we have not been able to falsify the Markov-chain hypothesis for Δz based on our statistics in all the investigated cases. Remarkably, the pure Ehrenfest Markov-chain theory is a good approximation for the gas, but does not work for the liquid.

B. Analysis of waiting times

The results of the simulations regarding the waiting time distribution are summarized in Table I. The Anderson-Darling statistics A^2 reported in the sixth column results from [29]

$$A^2 = \left\{ - \sum_{i=1}^n \frac{(2i-1)}{n} \{ \ln \Psi(\tau_{n+1-i}) + \ln [1 - \Psi(\tau_i)] \} - n \right\} \times \left(1 + \frac{0.6}{n} \right), \quad (7)$$

where $\Psi(\tau)$ denotes the survival function, a short name for

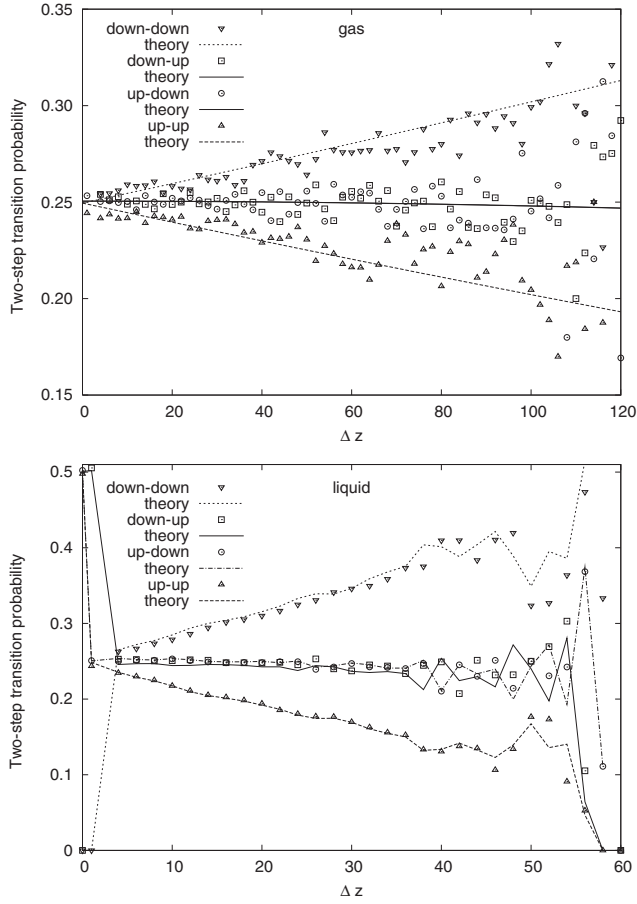


FIG. 5. Two-step transition probabilities $p_{dd}(\Delta z-4|\Delta z)$, $p_{du}(\Delta z|\Delta z)$, $p_{ud}(\Delta z|\Delta z)$, and $p_{uu}(\Delta z+4|\Delta z)$ for $\rho=0.05$, $T=1.6$ (gas, top) and $\rho=0.7$, $T=1.2$ (liquid, bottom), $N=1000$ without walls. The theoretical lines are the product of the two corresponding one-step transition probabilities—e.g., $p_{uu}(\Delta z+4|\Delta z)=p_u(\Delta z+4|\Delta z+2)p_u(\Delta z+2|\Delta z)$. We use the theoretical one-step transition probabilities for the gas and the observed ones for the liquid.

the complementary cumulative distribution function—i.e., the probability that waiting times are larger than τ . In Eq. (7) the waiting times are sorted: $\tau_1 \leq \tau_2 \leq \dots \leq \tau_n$. The limiting value at 1% significance for accepting the null hypothesis of exponentially distributed waiting times is 1.957. Therefore, the null hypothesis can be rejected in all cases with $\Delta t \geq 10^{-4}$. The average waiting time $\langle \tau \rangle$ and the standard deviation σ_τ of the observed distribution, reported in columns 7 and 8, must coincide for an exponential distribution. Even if their values are close, with the given statistics they cannot be considered equal. Figure 6 further illustrates this point; there, the *closest* case to an exponential for $N=1000$ is presented, $\rho=0.05$, $T=1.2$ without walls, as well as the *most distant* case, $\rho=0.7$, $T=1.6$ without walls. In both cases the points are the observed survival function $\Psi(\tau)$ and the dashed line is the exponential fit. A deviation from the exponential distribution is evident at first sight. It is important to remark that this is a one-parameter fit, since the average waiting time $\langle \tau \rangle$ is sufficient to fully determine the exponential distribution, with survival function $\Psi_{\text{exp}}(\tau)=\exp(-\tau/\langle \tau \rangle)$, corresponding to a given data set. In other words, the mere fact that in

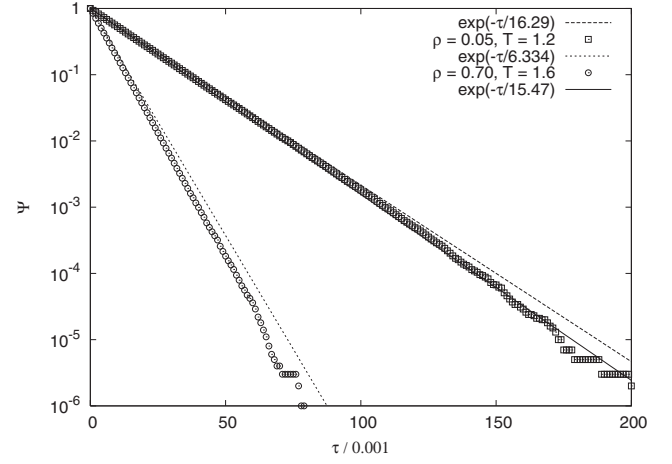


FIG. 6. $N=1000$, no walls. Comparison between the observed survival functions and the theoretical exponential survival functions (dashed lines) with the corresponding average waiting time $\langle \tau \rangle$, for the closest case (squares) and the most distant case (circles). The theoretical exponential survival function of the system with $N=2000$ and $\Delta t=10^{-5}$ is shown for reference (solid line).

log-linear scale the survival function is approximately a straight line is not sufficient to conclude that the observed distribution is exponential. In the four cases studied here, the presence of walls does not significantly affect the results.

However, the agreement improves if the integration time step Δt is reduced from 0.001 to 0.0002: for $\rho=0.05$, $T=1.2$ in the $N=2000$ system, A^2 drops from 2061 to 29.84 and $\langle \tau \rangle$ from 16.29 to 15.72; the lower value of $\langle \tau \rangle$ corresponds better to the observed survival function. The data change very little with respect to $\Delta t=0.001$ and are not shown in Fig. 6 to avoid cluttering. This indicates that the discrepancy is due to the finite integration time step and can be controlled through the latter. The hypothesis is confirmed reducing Δt further: for $\Delta t=10^{-4}$, $A^2=3.78$, and finally for $\Delta t=10^{-5}$, $A^2=0.686 < 1.957$ —i.e., the required threshold. The same trend is evident in the $N=100\,000$ system (see Fig.

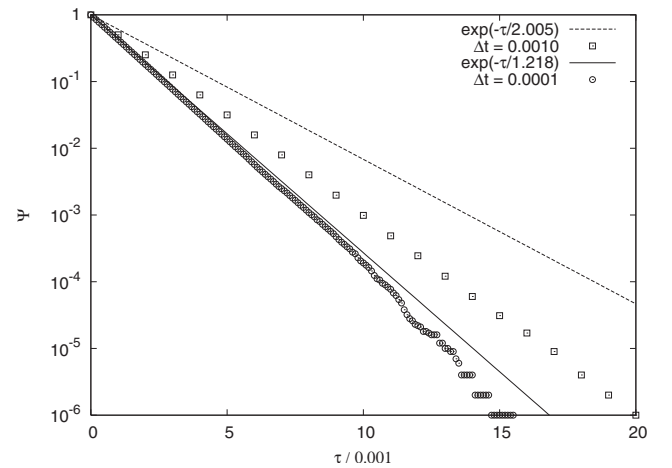


FIG. 7. Reducing the integration time step Δt improves the agreement between the observed survival function and an exponential function with a time constant equal to the average waiting time; system with $N=100\,000$, $\rho=0.05$, $T=1.2$.

TABLE I. For each integration time step Δt , number of atoms N , density ρ , and temperature T (a “w” before the N value indicates a system with walls in the x direction), this table gives the number of observed waiting times n , the values of the Anderson-Darling statistics A^2 [29], the average waiting time $\langle \tau \rangle$, and the standard deviation of waiting times σ_τ . Reduced units as defined in Sec. II are used throughout, with times divided by 0.001. The standard error on $\langle \tau \rangle$ is around 0.02 for $\rho=0.05$ and 0.006 for $\rho=0.70$. The standard error on σ_τ is around 0.02 for $\rho=0.05$ and 0.005 for $\rho=0.70$. Only significant digits are given in the table. The last digit of $\langle \tau \rangle$ and σ_τ is of the same order of magnitude as σ_τ/\sqrt{n} . See text for further explanations.

Δt	N	ρ	T	n	A^2	$\langle \tau \rangle$	σ_τ
1.0	1000	0.05	1.2	613 751	2061	16.29	15.79
1.0	w 1000	0.05	1.2	618 220	2096	16.18	15.69
1.0	1000	0.05	1.6	704 881	3038	14.19	13.67
1.0	w 1000	0.05	1.6	704 007	3031	14.20	13.68
1.0	1000	0.70	1.2	1 386 970	18 666	7.210	6.662
1.0	w 1000	0.70	1.2	1 407 654	19 428	7.104	6.562
1.0	1000	0.70	1.6	1 578 866	26 525	6.334	5.779
1.0	w 1000	0.70	1.6	1 565 301	25 835	6.389	5.841
1.0	500	0.70	1.6	675 876	2847	14.80	14.14
1.0	2000	0.70	1.6	1 561 554	25 704	6.404	5.856
0.2	2000	0.05	1.2	127 237	29.84	15.72	15.59
0.1	2000	0.05	1.2	64 617	3.78	15.48	15.46
0.01	2000	0.05	1.2	6 306	0.686	15.85	16.15
1.0	100 000	0.05	1.2	4 988 531	587 570	2.005	1.419
0.1	100 000	0.05	1.2	820 837	4534	1.218	1.166
0.1	100 000	0.70	1.6	2 043 142	52 278	0.4894	0.4369

7), though even smaller time steps would be necessary to reach the threshold because the average waiting time decreases inversely proportionally to the interface area.

As suggested by intuition, the average waiting time decreases with higher density and temperature, but also with a larger interface area S between the two parts of the box. Actually, the product $\langle \tau \rangle S$ is a constant for a given density and temperature. The survival functions of systems with dif-

ferent sizes overlap if $\langle \tau \rangle$ is multiplied by the interface area. This is shown in Fig. 8, where it is also clear that there are no changes due to the finite size of the system for $N \geq 1000$ (after correcting for the interface area, the survival function of $N=500$ is slightly displaced from all the others).

A better strategy than reducing the time step is to interpolate the time of the barrier crossing within a conventional time step: this way the waiting times can be determined with floating-point precision rather than as integer multiples of Δt , there will not be changes in $\Delta z > 2$, and it is likely that good results can be obtained with the maximum Δt compatible with energy conservation. Though we believe that the major effect of a finite Δt is through sampling, because without interpolation waiting times are systematically overestimated by a fraction of Δt , another effect is through the approximation of the true canonical dynamics. Indeed, with a soft potential this approximation can be reduced only in the limit of $\Delta t \rightarrow 0$, but it can be avoided completely in a system of hard spheres. Work along both lines, interpolation of the waiting times and hard spheres, is in progress.

IV. CONCLUSIONS

In summary, we have studied the Ehrenfest urn with a realistic model of condensed matter, the Lennard-Jones fluid. The Ehrenfest urn has been defined by Kac as the best model ever envisaged in statistical mechanics [30], yet it has also been criticized as a marvellous exercise too far removed from reality [11]. On the 100th anniversary of Ehrenfest and Ehrenfest’s original paper, we have shown that this criticism

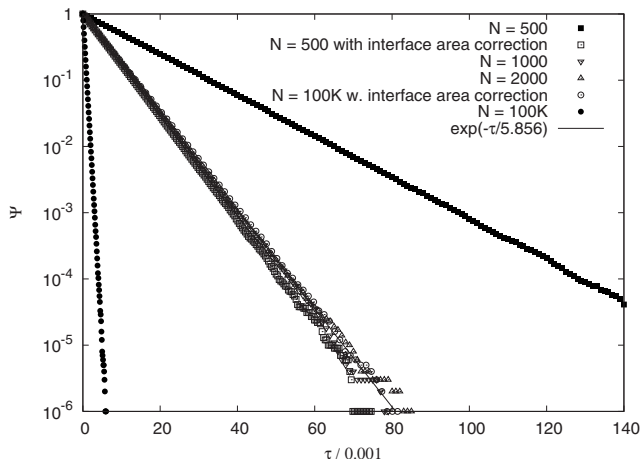


FIG. 8. Survival functions for $\rho=0.7$, $T=1.6$ and different system sizes. They overlap if $\langle \tau \rangle$ is multiplied by the ratio of the interface area to the interface area of the systems with $N=1000$ or 2000 (which are equal because the former is the only one with a cubic unit box, while all the others have side ratios of 2:1:1). A finite-size effect is noticeable only in the smallest system.

is unjustified, since computer “experiments” allow one to follow the motion of molecules and to count how many are on one side of a box or the other at a given time. We have studied the behavior of the pure-jump stochastic process $\Delta z = |P - Q|$ induced by the deterministic dynamics under coarse graining, where P is the number of fluid particles on the left-hand side of the simulation box and Q that on the right-hand side. We have performed simulations with periodic boundary conditions and with walls in one direction, finding that the presence of walls does not affect the results. We have found that in the gas phase the observed transition probabilities follow the predictions of the Ehrenfest theory and that the waiting time distribution between successive variations of Δz , though not strictly exponential, becomes closer to an exponential reducing the integration time step; therefore, in the limit of a vanishing time step, we found that the corresponding pure-jump process is Markovian. In the

future, we plan to further study the stochastic process presented here, interpolating the waiting times to higher precision, simulating systems of hard spheres to avoid approximations in the dynamics due to a finite integration time step, and investigating the pure-jump process in a coarse-grained configuration space as required by the theory developed by Boltzmann. Our results so far corroborate the Markovian hypothesis lying at the foundation of statistical mechanics [8].

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