Fluctuations in partitioning systems with few degrees of freedom

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We study the behavior of a moving wall in contact with a particle gas and subjected to an external force. We compare the fluctuations of the system observed in the microcanonical and canonical ensembles, by varying the number of particles. Static and dynamic correlations signal significant differences between the two ensembles. Furthermore, velocity-velocity correlations of the moving wall present a complex two-time relaxation that cannot be reproduced by a standard Langevin-like description. Quite remarkably, increasing the number of gas particles in an elongated geometry, we find a typical time scale, related to the interaction between the partitioning wall and the particles, which grows macroscopically.

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I. INTRODUCTION

Macroscopic objects contain at least $N = O(10^{20})$ particles; therefore, in the mathematical modeling, one can safely assume $N \to \infty$ and study their asymptotic features (e.g., the thermodynamics limit). As a consequence of such a huge value of N, up until a few decades ago statistical mechanics had been devoted almost only to the study of systems with many degrees of freedom [1]. In contrast, present day instrumentation allows us to manipulate (and sometimes control) small systems at the microscale and even the nanoscale; it is not necessary to emphasize the practical relevance of small systems [2,3].

In order to deal with systems with a small number of particles, say, $O(10^2)$ or less, we are forced to (re)consider in detail some aspects of statistical mechanics [4] that for macroscopic bodies are not very relevant. For instance, in large systems the fluctuations are always relatively negligible and apparently irrelevant [5]. In a similar way, for macroscopic objects, there are neither particular problems for the definition of temperature [6] nor significant differences using different statistical ensembles (e.g., microcanonical or canonical).

Among the physical systems relevant for the nanosciences we can mention the class of partitioning objects containing an extra degree of freedom (a wall) that separates the system into subsystems. A paradigmatic example is given by the adiabatic piston [7–11]: a system of N particles of mass m (e.g., an ideal gas) in a container of length L and cross section A, separated in two regions by a movable wall (the piston) of mass M. The walls of the container are supposed to be perfect insulators preventing any mass or heat exchanges with the exterior. Gas particles undergo purely elastic collisions with the piston and the walls and the piston is constrained to move along one axis. If at initial time the temperatures T_L,T_R and pressures P_L,P_R in the left and right parts do not coincide, the system shows a rather rich phenomenology (depending on M/m, N/L, etc.) in the approach to the mechanical and thermodynamic equilibrium.

A physical version of the adiabatic piston is a big Brownian particle sliding along a microtubule filled with particles [12]. The authors of Ref. [12] showed how the presence of the wall is able to induce, even in the equilibrium state, rather complex (and slow) dynamical behavior.

Our paper is devoted to the statistical mechanics of a system similar to a piston where particles are confined in a tube with a nonfixed wall, on which an external force acts (see Fig. 1). The pressure on the piston due to the interaction with the gas particles on one side is balanced by the external force, so the piston reaches a stationary state. We are interested in the study of piston fluctuations (of position and velocity) around the equilibrium state. In the case of noninteracting particles it is possible to find in an exact way the equilibrium properties of the system in both microcanonical and canonical ensembles (this latter case is realized by putting a thermostat on the fixed

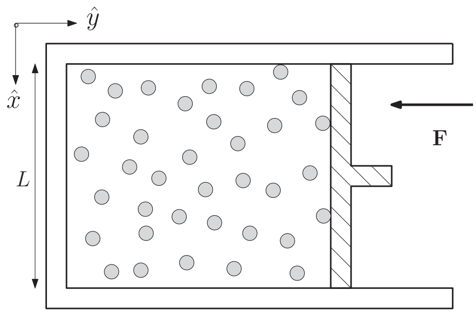

FIG. 1. Sketch of the piston model. A gas of particles is confined by a moving wall that is subjected to a constant external force.

wall, which thermalizes particles colliding with the wall). One obtains that, even in the limit $N \gg 1$, the fluctuations of the wall position are different in the canonical and microcanonical ensembles. An important consequence of such a difference, which holds also for the interacting particles, is that the correlation function (of the velocity) $C(t)$ must be different in the two ensembles.

Numerical simulations show a nontrivial behavior of $C(t)$ with a negative minimum around a characteristic time $\tau(N)$ increasing linearly with N. A comparison between the numerical results and an appropriate Langevin equation shows how even for large N the presence of the wall has nontrivial consequences that can have a role in an effective modeling of the system.

The paper is organized as follows. Section II describes the model in detail and presents the analytical results for the ideal gas case. In Sec. III we report the results of molecular dynamics simulations in the interacting case. Section IV is devoted to the derivation of an effective Langevin equation for describing the dynamics of the piston. In Sec. V a summary is given and conclusions are drawn. Two Appendixes provide details about the computations.

II. MODEL

We consider a two-dimensional system composed of a gas of N pointlike particles with mass m, positions $\mathbf{x}_i = \{x_i, y_i\}$, and momentum $\mathbf{p}_i$, with $i = 1, \ldots, N$, contained in a rectangular box with one moving adiabatic wall of length L (hereafter referred to as the piston). The position of the piston is denoted by Y and its momentum and mass are P and M, respectively (see Fig. 1 for a visual explanation). An external force $\mathbf{F} = -F \cdot \hat{y}$, directed along the horizontal axis $\hat{y}$, acts on the piston, which is also subject to the collisions with the particles. In the tubular geometry that we consider, in which the size of the system is increased anisotropically only along one direction when adding particles, the piston plays the role of a partitioning object with respect to the particle gas, namely, its position determines the volume available for the gas. This system has been studied in [6] as an effective thermometer model. In the following the particle-particle and particle-piston interactions are described in a Hamiltonian (conservative) context and the piston can slide without dissipation along the y axis. The case of dissipative interactions, inducing nonequilibrium behaviors, of similar systems have been studied, for instance, in [13–18].

We start by considering the case of a noninteracting gas, so the Hamiltonian of the system reads

$$\mathcal{H} = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \frac{P^2}{2M} + FY, \tag{1}$$

with geometrical constraints

$$Y > 0, \quad 0 < x_i < L, \quad 0 < y_i < Y. \tag{2}$$

We are interested in the study of the behavior of fluctuations for a varying number of gas particles and in particular in the comparison between the microcanonical and canonical ensembles. As shown in Appendix A, in the microcanonical ensemble the temperature of the system is related to the energy E of the system by the relation

$$k_B T = \left(\frac{\partial \ln \Sigma(E)}{\partial E}\right)^{-1} = \frac{E}{2N + \frac{3}{2}}, \tag{3}$$

where

$$\Sigma(E) = \int_{\mathcal{H}<E} d^N\mathbf{x}\, d^N\mathbf{p}\, dY\, dP \tag{4}$$

is the phase space volume and k_B the Boltzmann constant. The static properties of this system, average position $\langle Y \rangle$, and variance $\sigma_Y^2 = \langle Y^2 \rangle - \langle Y \rangle^2$ can be readily obtained (see Appendix A), yielding

$$\langle Y \rangle = \frac{(N+1)k_B T}{F}, \tag{5}$$

$$\sigma_Y^2 = \frac{(N+1/2)(N+1)}{2N+5/2}\left(\frac{k_B T}{F}\right)^2. \tag{6}$$

Let us parenthetically remark on the definition of temperature. Equation (3) is not a unique possibility; another way is via the formula

$$k_B T' = \left(\frac{\partial \ln \omega(E)}{\partial E}\right)^{-1}, \tag{7}$$

where $\omega(E) = \frac{\partial \Sigma(E)}{\partial E}$. There are cases in which T and T' can be different and in particular T' can be negative, e.g., in the case of point vortex systems [19]. On the other hand, in a perfect gas it is easy to see that the two definitions are equivalent for $N \gg 1$ since $T - T' = O(\frac{1}{N})$ [20]; this result also holds for weakly interacting systems.

Analogous results can be obtained for the canonical case, where the system is in contact with a reservoir at temperature T. In this case, the energy of the system is

$$E = -\frac{\partial \ln Z(\beta)}{\partial \beta} = \left(2N + \frac{2}{3}\right)k_B T, \tag{8}$$

where

$$Z(\beta) = \int d^N\mathbf{x}\, d^N\mathbf{p}\, dY\, dP\, e^{-\beta\mathcal{H}} \tag{9}$$

TABLE I. Comparison of average position and variance in the microcanonical and canonical ensembles.

Observable	Canonical	Microcanonical
temperature	T	$\frac{E}{2Nk_B}$
$\langle Y\rangle$	$\frac{Nk_BT}{F}$	$\frac{E}{2F}=\frac{Nk_BT}{F}$
σ_Y^2	$\frac{N(k_BT)^2}{F^2}$	$\frac{E^2}{8NF^2}=\frac{N(k_BT)^2}{2F^2}$

and $\beta=1/k_BT$ is the inverse temperature. The average position and variance σ_Y^2 read (see Appendix A)

$$\langle Y\rangle=\frac{(N+1)k_BT}{F}, \tag{10}$$

$$\sigma_Y^2=(N+1)\left(\frac{k_BT}{F}\right)^2. \tag{11}$$

In order to compare the results for static quantities $\langle Y\rangle$ and σ_Y^2 in the two ensembles, for each temperature T in the canonical ensemble we consider the corresponding energy in the microcanonical, such that $T=E/2Nk_B$, in the limit of a large number of particles $N\gg 1$. While the average position is always the same, from Eqs. (6) and (11) one observes that fluctuations differ by a factor 1/2, also in the large-N limit. In Table I we summarize these findings.

The equivalence of ensembles in the thermodynamic limit is expected only for average values and not for fluctuations [4,21]. Indeed, the observed discrepancy is explained by noting that the variance in the canonical ensemble can be expressed as the sum of two contributions, namely, a term that corresponds to the variance of the piston in the microcanonical ensemble at fixed energy plus a term corresponding to energy fluctuations at fixed temperature:

$$\sigma_Y^2(T)=\alpha\sigma_E^2(T)+\sigma_Y^2(E)|_{E=\langle E\rangle_\beta}, \tag{12}$$

where $\alpha=1/4F^2+O(1/N)$ and $\sigma_E^2=\langle\mathcal{H}^2\rangle-E^2$. Therefore, for $N\gg 1$, since $\sigma_E^2(T)\approx 2N(k_BT)^2$, one has $\sigma_Y^2(T)=2\sigma_Y^2(E)|_{E=2Nk_BT}$.

Let us briefly digress on terminology. With the term "canonical ensemble" we mean the system with the Hamiltonian in Eqs. (1) and (2) (in the following we will include also the interactions among the particles) interacting with a thermal bath at temperature T. Noting that the pressure is nothing but F/L, one can then say that we are dealing with an ensemble at fixed temperature and fixed pressure for the system without the terms FX and $P^2/2M$ in the Hamiltonian [21]. In a similar way our microcanonical ensemble corresponds to an ensemble with fixed enthalpy for the system without the terms FX and $P^2/2M$ in the Hamiltonian. We prefer the terms canonical and microcanonical because they put the dynamical variables describing the wall on the same level as that for the particles. Let us note that the mass of the piston is important for the dynamical properties.

The above results on the fluctuations immediately produce two important consequences on the dynamical correlations in the two ensembles. First, notice that the finite value of the variance σ_Y^2 in both cases for finite N implies that the diffusion coefficient D of the piston is zero, implying that the piston remains confined. Second, the difference in the static fluctuations has repercussions on the shape of the velocity-velocity fluctuations in the canonical and microcanonical ensembles. Let us note that

$$\sigma_Y^2=\langle(Y-\langle Y\rangle)^2\rangle=\int_0^\infty\int_0^\infty\langle V(t')V(t'')\rangle dt'dt'', \tag{13}$$

where $V(t)$ is the velocity of the piston. Since σ_Y^2 are different in the canonical and microcanonical ensembles, also the correlation $\langle V(t)V(0)\rangle$ must be different. These issues will be addressed in the next section, in the case of interacting gas.

Exactly the same considerations about the difference of fluctuations in the canonical and microcanonical ensembles hold in the case that a different thermodynamic limit is considered, in which the size of the piston is increased isotropically. In this case, in order to have that for each value of N the shape of the gas compartment is isotropic, namely, $\langle Y\rangle=L$, and that the density $\rho=N/L^2$ and the pressure $p=F/L$ are constant, we need the scaling $F\sim\sqrt{N}$ for the force acting on the piston. If we insert such scaling for F in Eqs. (6) and (11), we find that increasing isotropically the size of the compartment, at variance with the tubular geometry, the mean square displacement σ_Y^2 of the partitioning wall becomes asymptotically constant for increasing N in the two ensembles. On the contrary, the factor 2 by which canonical and microcanonical fluctuations differ remains the same. The comparison between the two different thermodynamic limits on the one hand tell us that the result of the difference in canonical and microcanonical fluctuations is robust and on the other hand allows us to point out the peculiarities of the tubular geometry.

III. NUMERICAL SIMULATIONS FOR THE INTERACTING CASE

In order to understand whether the previous results are peculiar to the noninteracting case and to study a more realistic case, we perform molecular dynamics simulations of the system with an interacting particle gas. We consider a repulsive interaction potential $V(\mathbf{r})$ for soft disks, with cutoff r_c,

$$V(\mathbf{r})=\begin{cases}V_0\left[\left(\frac{r_0}{r}\right)^{12}-\left(\frac{r_0}{r_c}\right)^{12}+12\left(\frac{r_0}{r_c}\right)^{12}\left(\frac{r}{r_c}-1\right)\right] & \text{for } r<r_c\\ 0 & \text{for } r>r_c,\end{cases} \tag{14}$$

where $r=|\mathbf{r}|$ is the distance between particles, V_0 is the potential intensity, and r_0 is the average interaction range. The same potential also describes the interaction of particles with walls. In the simulations of the canonical ensemble the coupling with the *reservoir* at temperature T is implemented in the following way. We consider that the side of the box opposite to the piston acts as a thermostat, so that when a particle enters the interaction region with the wall, namely, its distance from the wall is smaller than r_0, the velocity changes along the y axis according to the Maxwellian distribution $p(v_y)\propto v_y\exp(-v_y^2/2mk_BT)$, for $v_y>0$ [22]. The study of the system upon varying N is performed by retaining a tubular geometry, namely, keeping the length L and the force F constant and letting the equilibrium position $\langle Y\rangle$ increase accordingly, so that the gas density remains fixed. The results described here are not related to a specific interaction. Indeed, we also studied the case of a stronger interaction potential

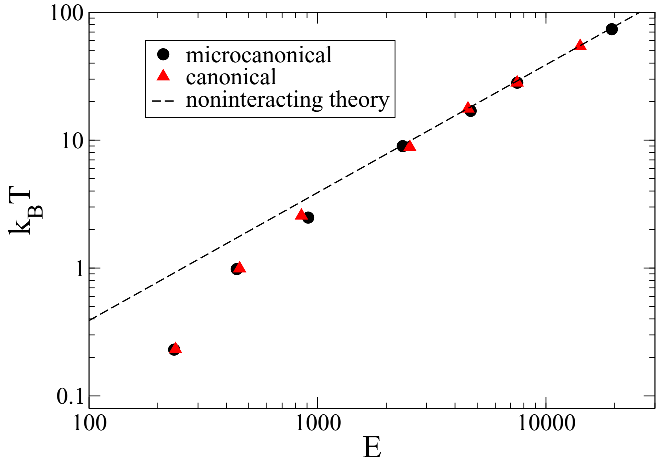

FIG. 2. (Color online) Temperature $k_B T$ (in the microcanonical ensemble it is $M\langle V^2\rangle$) plotted as a function of energy E (in the canonical ensemble $E = \langle\mathcal{H}\rangle$) for $N = 128$. The dashed line represents the theoretical result for noninteracting particles $k_B T = E/(2N + 3/2)$, which is expected to hold for high temperatures. The other parameters in the simulations are $L = 10$, $F = 10$, $m = 1$, and $M = 128$.

$V(r) \sim r^{-64}$, which at low density reproduces the behavior of hard-disk statistics [23], finding analogous results.

We start the numerical study of this interacting case by checking the validity of the relation (3). In Fig. 2 we plot the temperature T as a function of the energy E in the microcanonical and canonical ensembles. The temperature is computed as $k_B T = M\langle V^2\rangle$, whereas energy is $E = \langle\mathcal{H}\rangle$. As expected, the theoretical relation (3) derived in the noninteracting system is valid at high temperatures, where interactions become negligible. In Fig. 3 we report the average values of the piston position and its variance in the two ensembles. Notice that also in this case the analytical predictions (5) and (10) hold in the high energy (or temperature) regions. It is interesting that also in the interacting case the factor 1/2 between the σ_Y^2 in the canonical and microcanonical ensembles is still present (see Fig. 4).

Interesting behaviors are also found for the dynamical properties of this system. Indeed, differences in the fluctuations between microcanonical and canonical are evident from the study of correlation functions. In particular, in Fig. 5 we compare the behavior of the normalized velocity autocorrelation function of the piston $C(t) = \langle V(t)V(0)\rangle/\langle V(0)V(0)\rangle$ for different values of N. First, one clearly observes that, as expected from the static results, fluctuations are larger in the canonical ensemble, namely, the system is less correlated than in the microcanonical ensemble. Moreover, let us notice the nontrivial shape of $C(t)$. For small N one has a damped oscillatory relaxation, while for increasing N a peculiar behavior emerges: After the first stage of relaxation, governed by a simple exponential decay, at later times a negative bump occurs, signaling the presence of another time scale in the system. This negative contribution to the correlation is necessary for the vanishing of the diffusion constant: $\int_0^\infty C(t)dt$ must be zero.

From the above results for $C(t)$, a two-time scenario emerges. We have the time τ_0, characterizing the first

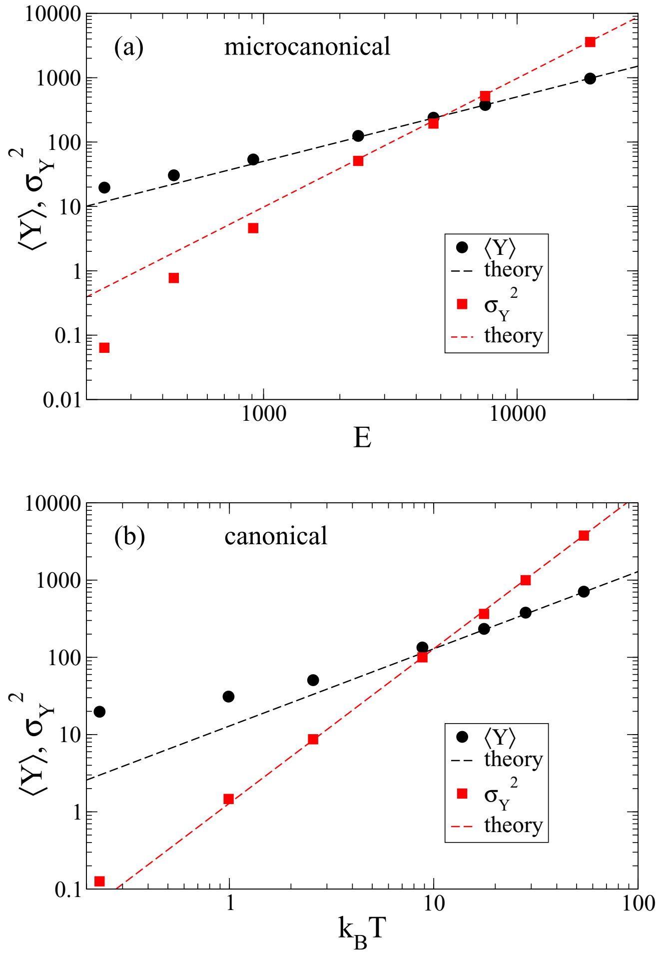

FIG. 3. (Color online) (a) Average position $\langle Y\rangle$ and variance σ_Y^2 plotted as a function of energy E in the microcanonical ensemble with $N = 128$. Dashed lines represent the theoretical results for the noninteracting gas $\langle Y\rangle = (N+1)E/F(2N+3/2)$ and $\sigma_Y^2 = (N+1)(N+1/2)/[(2N+5/2)(2N+3/2)^2](E/F)^2$. (b) Same quantities as a function of $k_B T$ in the canonical ensemble. The theoretical results for the noninteracting gas are $\langle Y\rangle = (N+1)k_B T/F$ and $\sigma_Y^2 = (N+1)(k_B T)^2/F^2$. The other parameters in the simulations are $L = 10$, $F = 10$, $m = 1$, and $M = 128$.

exponential decay, empirically defined as the time necessary to cross the zero axis for the first time. In addition, we have the time $\tau(N)$ where the negative bump occurs. The first decay of the velocity correlation function $C(t)$ saturates upon increasing the number of particles and so the time τ_0 tends to a constant value, independent of N [see Fig. 6(a), where τ_0 is plotted as a function of N on a semilogarithmic scale, for both the microcanonical and canonical ensembles]. On the other hand, we find that the second time scale τ depends linearly on N, as shown in Fig. 6(b), where $C(t)$ is plotted as a function of t/N. In the inset we also plot $\tau(N)$ as a function of N on a log-log scale for the canonical ensemble, showing the linear increase with N (analogous results are observed for the microcanonical ensemble). As discussed in the next section, such a peculiar behavior, induced by the presence of the partitioning piston, cannot be easily described by a standard Langevin-like approach.

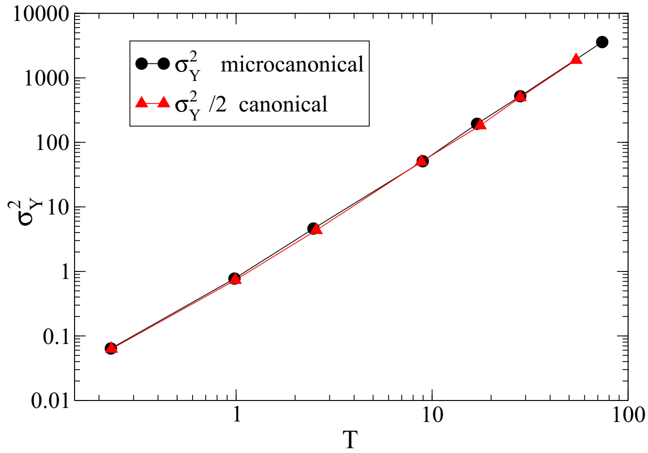

FIG. 4. (Color online) Variance σ_Y^2 plotted as a function of $k_B T$ in the canonical and microcanonical ensembles (in the latter case we consider simulations at constant energy and the temperature is obtained from $k_B T = M\langle V^2\rangle_E$) for $N = 128$. The other parameters in the simulations are $L = 10$, $F = 10$, $m = 1$, and $M = 128$.

IV. LANGEVIN EQUATION

In the limit of N and M very large, the relaxation times of the piston and of the gas particles are well separated and one may consider the gas particles weakly perturbed by the presence of the piston. Within this strong assumption, the gas distribution is fixed and independent of the motion of the piston and the dynamics can be described by a master equation for the probability density function $P(V,Y,t)$ of the velocity V of the piston at position Y at time t. In particular, for the first moment of this distribution, it is possible to write down the following equation (for the details refer to Appendix B):

$$\frac{d\langle V\rangle}{dt} = \langle F_{\rm coll}(Y,V)\rangle. \tag{15}$$

Then the fluctuations around the equilibrium position ($Y \simeq Y_{eq}$ and $V \simeq 0$) are described by expanding up to first order the right-hand side of Eq. (15), obtaining

$$\frac{dV(t)}{dt} = -k_N y - \gamma V + \xi(t), \tag{16}$$

where the displacement $y \equiv Y - Y_{eq}$ has been introduced. The parameters k_N and γ can be calculated by means of kinetic theory and their explicit expressions are written in Eq. (B11). One must notice that in Eq. (16) a noise term $\xi(t)$ has been added, whose expression cannot be directly derived from Eq. (15) for the mean velocity. Actually, the correlation of the noise term can be determined by exploiting the equipartition theorem valid for equilibrium dynamics. By requiring Maxwellian statistics for the stationary $P(V)$, it is well known that $\xi(t)$ must be white noise with variance

$$\langle\xi(t)\xi(t')\rangle = 2\gamma T\delta(t - t'). \tag{17}$$

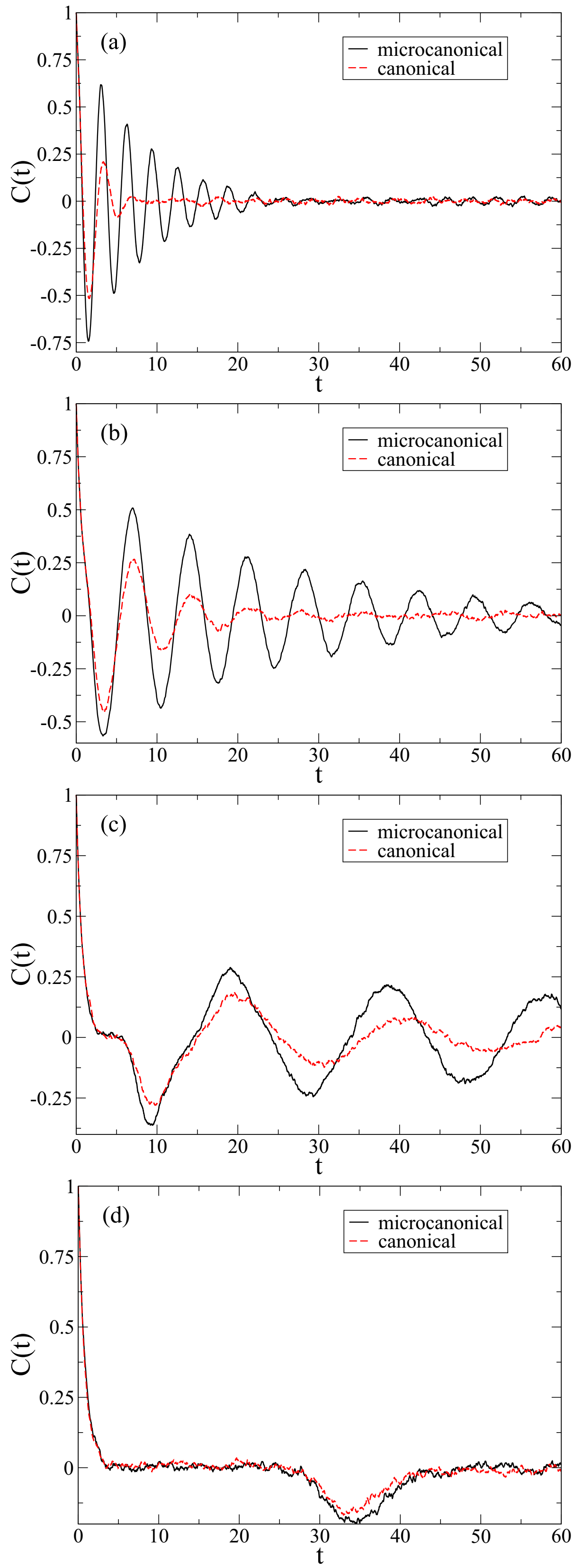

FIG. 5. (Color online) Velocity autocorrelation functions of the piston in the microcanonical and canonical ensembles for (a) $N = 16$, (b) $N = 64$, (c) $N = 256$, and (d) $N = 1024$. The other parameters are $L = 30$, $F = 150$, $T = 10$, $m = 1$, and $M = 50$.

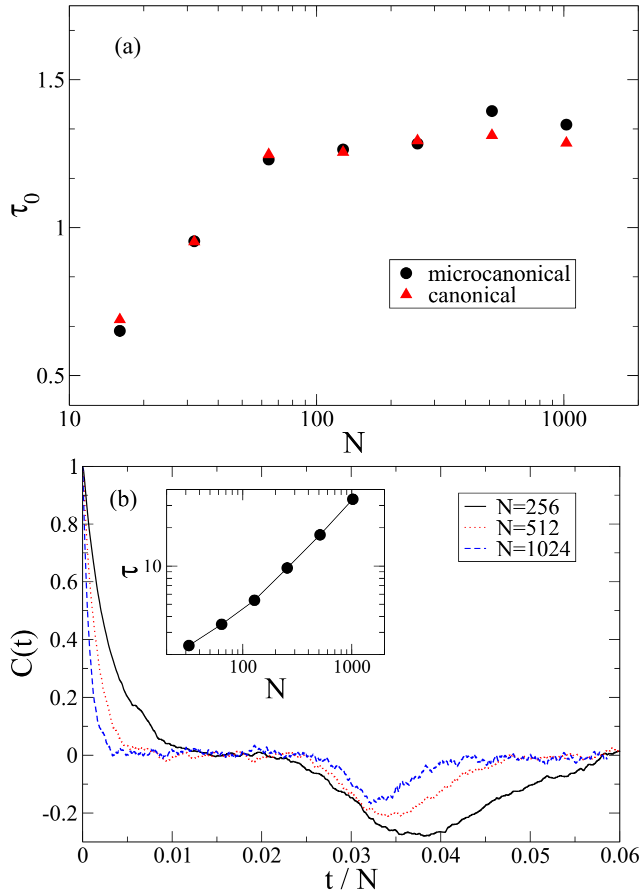

FIG. 6. (Color online) (a) First relaxation time τ_0 of the piston velocity correlation for different values of N, in the microcanonical (black circles) and canonical (red squares) ensemble with parameters $M = 50$, $F = 150$, $L = 30$, and $k_B T = 10$. Notice that the first relaxation saturates for large N and the time τ_0 reaches a constant value in both the canonical and microcanonical ensembles. (b) Velocity correlation functions as a function of time rescaled by N in the canonical ensemble with same parameters. In the inset the time τ shows a linear dependence on N for large N.

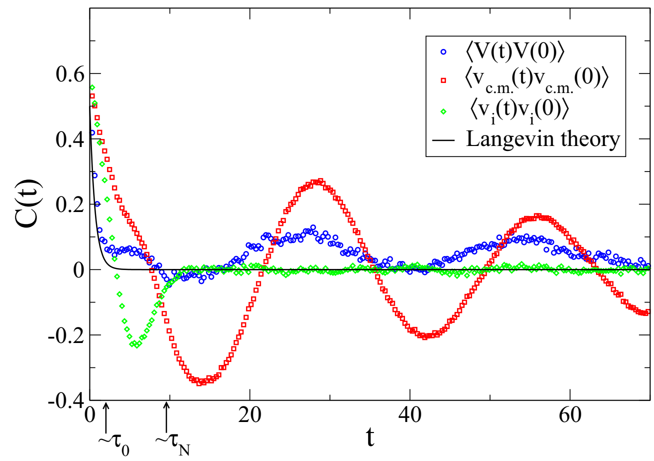

FIG. 7. (Color online) Autocorrelation of different observables in the case of a piston with noninteracting particles (canonical ensemble) measured in numerical simulations and the Langevin approximation for the piston velocity correlation (black line). It is possible to observe how the oscillation in the autocorrelation of the piston velocity $\langle V(t)V(0)\rangle$ (blue circles) are in phase with the one of the center of mass of the gas particles $\langle v_{\mathrm{c.m.}}(t)v_{\mathrm{c.m.}}(0)\rangle$ (red squares). Green diamonds represent the autocorrelation of a single-particle velocity $\langle v_i(t)v_i(0)\rangle$. All the correlations are normalized to one for $t = 0$. The parameters are $F = 150$, $T = 10$, $M = 50$, and $N = 500$.

From the linearity of Eq. (16) it is possible to calculate the autocorrelation of velocity, obtaining

$$\langle V(t)V(0)\rangle = \frac{T}{M}e^{-\gamma t/2}\left[\cosh\left(\frac{\Delta}{2}t\right) - \frac{\gamma \sinh\left(\frac{\Delta}{2}t\right)}{\Delta}\right], \tag{18}$$

where we introduced the parameter $\Delta = \sqrt{\gamma^2 - 4k_N}$, which rules the passage between the underdamped and overdamped regimes. More specifically, if $\frac{Nm}{m+M} > \frac{\pi}{2}$, the system is overdamped; otherwise the system is underdamped.

Making a comparison between Eq. (18) and the numerical experiments presented in Fig. 5, it appears evident that the Langevin equation is able to capture, for N large, only the small time relaxation $\tau_0 \simeq \gamma^{-1}$, while it is unable to detect the oscillation of $\langle V(t)V(0)\rangle$, which appears for times $\tau(N) \sim N$. We report in Fig. 7 the explicit comparison between the Langevin approximation (black curve) and the piston velocity correlation (red curve) in the noninteracting case. The same mismatch between analytical prediction and numerical results is observed also for interacting particles. The oscillations presented by $\langle V(t)V(0)\rangle$ are related to the interplay mechanism between the moving wall and a collective mode of the gas particles, which makes the assumption of Markovian nature fail. We note how this phenomenon is quite general and it is present also in the case of noninteracting gas particles. In order to verify this point, one can analyze a natural collective variable of the gas, i.e., the center of mass velocity $v_{\mathrm{c.m.}}(t) \equiv \frac{1}{N}\sum v_i(t)$. In the simpler case of a noninteracting gas confined in a fixed volume, the autocorrelation $\langle v_{\mathrm{c.m.}}(t)v_{\mathrm{c.m.}}(0)\rangle$ would be trivially equal to the one of a single particle in the gas. On the contrary, this is not true anymore with the presence of the piston since the different particles of the gas are strongly correlated with each other via the mutual interaction piston or border. The time scale of this process is very close to $\tau(N)$, as can be observed in Fig. 7. Such a time scale is completely hidden if one consider only the single-particle autocorrelation $\langle v_i(t)v_i(0)\rangle$.

V. CONCLUSION

In the present work we have shown, with analytical calculations in the ideal gas case and with simulations for interacting particles, that the fluctuations in the canonical and microcanonical ensembles [24] show relevant differences when a partitioning object, such as a moving wall, is introduced. The relevant points that we have highlighted are the following. First, we have shown that the interaction with the partitioning object induces nontrivial correlations among the particles even in the ideal gas approximation (see Fig. 7 in Sec. IV), irrespectively of the ensemble, canonical or microcanonical, where the dynamics is studied. Then we have shown that the Langevin approach to the dynamics of the piston captures only partially the physics of the system. The Langevin equation correctly predicts only the fast time scale, namely, $\tau_0 \sim \gamma^{-1}$, but fails completely to catch the slower one, which grows linearly with the number of particles in the partitioned system $\tau(N) \sim N$. This second time scale is produced by nontrivial correlation between the velocity of the gas particles and the one of the piston, which is present, quite remarkably, also in the case of noninteracting particles, as shown in Fig. 7.

We recall that the macroscopic growth of $\tau(N)$ is related to the particular tubular geometry of the problem, where the size of the gas compartment is increased only in one direction. Notwithstanding the different behavior of the largest time scale, the factor 2 difference between canonical and microcanonical fluctuations of the partitioning object σ_Y^2 is independent of how the thermodynamic limit is taken, which is clear from Eqs. (6) and (11). We can therefore conclude that partitioning geometries with a single macroscopic degree of freedom that is effectively coupled to the motion of all the microscopic constituents of the system represent an eligible framework in which to study the dynamical properties of small systems.

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APPENDIX A

1. Microcanonical ensemble

In the microcanonical ensemble at energy E, the invariant measure is nonzero only on the hypersurface of constant energy S_E. If $\mathcal{M}$ is a subset of S_E and $d\sigma$ is the infinitesimal surface element

$$\mathbb{P}(x \in \mathcal{M} \subseteq S_E) = \int_{\mathcal{M}} \frac{d\sigma}{\omega(E)} \frac{1}{|\nabla \mathcal{H}|}, \quad \text{(A1)}$$

where $\omega(E) = \partial \Sigma(E)/\partial E$. In order to derive the expression of the temperature of the system as a function of the energy, we must compute $\Sigma(E)$. This quantity is given by

$$\Sigma(E) = \int_{\mathcal{H}<E} d^N x\, d^N y\, dY\, d^N \mathbf{p}\, dP$$
$$= L^N \int_{\sum_i |\mathbf{p}_i|^2/2m + P^2/2M + FY < E} d^N y\, dY\, d^N \mathbf{p}\, dP. \quad \text{(A2)}$$

Recalling that the volume of a D-dimensional sphere of radius R is

$$V(R) = \int_{\sum_i x_i^2 < R^2} d^D x = \frac{\pi^{D/2}}{\Gamma\left(\frac{D}{2}+1\right)} R^D,$$

where $\Gamma(x)$ is the Euler Gamma, from Eq. (A2) we obtain

$$\Sigma(E) = (2m)^N \sqrt{2M} L^N \frac{\pi^{N+1/2}}{\Gamma\left(N+\frac{3}{2}\right)} \times \int_0^Y d^N y \int_0^{E/F} dY (E - FY)^{N+1/2}$$

$$= (2m)^N \frac{\sqrt{2M}}{F} \left(\frac{L}{F}\right)^N \frac{\pi^{N+1/2}}{\Gamma\left(N+\frac{3}{2}\right)} E^{2N+3/2} \times \int_0^1 dx\, x^N (1-x)^{N+1/2} \quad \text{(A3)}$$

and eventually

$$\Sigma(E) = (2m)^N \frac{\sqrt{2M} L^N}{F^{N+1}} \pi^{N+1/2} \frac{\Gamma(N+1)}{\Gamma\left(2N+\frac{5}{2}\right)} E^{2N+3/2} \quad \text{(A4)}$$

and

$$\omega(E) = (2m)^N \frac{\sqrt{2M} L^N}{F^{N+1}} \pi^{N+1/2} \frac{\Gamma(N+1)}{\Gamma\left(2N+\frac{3}{2}\right)} E^{2N+1/2}. \quad \text{(A5)}$$

Now we can compute the temperature of the system using the relation $S = k_B \ln \Sigma(E)$, namely,

$$k_B T = k_B \left(\frac{\partial S}{\partial E}\right)^{-1} = \frac{\Sigma(E)}{\omega(E)} = \frac{E}{2N+\frac{3}{2}}. \quad \text{(A6)}$$

Using alternative definitions of S, e.g., $S = k_B \ln \omega(E)$ or $S = k_B \ln \Gamma_{\Delta E}(E)$, where $\Gamma_{\Delta E}(E) = \Sigma(E+\Delta E) - \Sigma(E) \simeq \omega(E)\Delta E$, where ΔE is the tolerance on E, for $N \gg 1$ one has negligible differences [20].

We are interested in the probability density function of the position of the piston Y. Observing that for a generic phase space function $A(\mathbf{X})$ in the microcanonical ensemble one has [25]

$$\rho_A(a) = \frac{1}{\omega(E)} \frac{\partial}{\partial E} \mathcal{I}(E,a), \quad \text{(A7)}$$

where

$$\mathcal{I}(E,a) = \int_{\mathcal{H}<E} \delta(A(\mathbf{x}) - a) d\mathbf{x}, \quad \text{(A8)}$$

setting $A(\mathbf{X}) = Y$ one readily obtains

$$I(E, Y = \tilde{Y}) = \int_{H<E} dY\, d^N x\, d^N y\, d^N \mathbf{p}_i dp\, \delta(Y - \tilde{Y})$$
$$= (2m)^N \sqrt{2M} L^N \frac{\pi^{N+1/2}}{\Gamma\left(N+\frac{3}{2}\right)} \tilde{Y}^N (E - F\tilde{Y})^{N+1/2} \quad \text{(A9)}$$

for $0 < \tilde{Y} < E/F$; therefore,

$$\rho_E(Y) = \frac{1}{\omega(E)} \frac{\partial I}{\partial E} = \frac{\Gamma\left(2N+\frac{3}{2}\right)}{\Gamma\left(N+\frac{1}{2}\right)\Gamma(N+1)} \times \frac{F}{E} \left(\frac{FY}{E}\right)^N \left(1 - \frac{FY}{E}\right)^{N-1/2}. \quad \text{(A10)}$$

From the above result we obtain

$$\langle Y \rangle = \frac{(N+1) k_B T}{F} \quad \text{(A11)}$$

and

$$\sigma_Y^2 = \frac{\left(N+\frac{1}{2}\right)(N+1)}{2N+\frac{5}{2}} \left(\frac{k_B T}{F}\right)^2. \quad \text{(A12)}$$

where, in these two last equations, we used Eq. (A6) to express $\langle Y \rangle$ and σ_Y^2 as functions of T instead of E.

2. Canonical ensemble

In the canonical ensemble at constant temperature T with $\beta = 1/k_B T$ the partition function of the system is given by

$$Z = \int d^N x\, d^N y\, dY\, d^N \mathbf{p}\, dP\, e^{-\beta\mathcal{H}} = \left(\frac{2}{\pi}\right)^{N+1/2} N!\, m^N \sqrt{M} \beta^{-(2N+3/2)} F^{-(N+1)}. \quad \text{(A13)}$$

We can easily compute the mean energy of the system

$$E = \langle\mathcal{H}\rangle = -\frac{\partial \ln Z}{\partial\beta} = \left(2N + \frac{3}{2}\right) k_B T. \quad \text{(A14)}$$

Now we want to find the probability distribution function of the position of the piston Y: Starting from

$$\rho_\beta(Y,\{y_i\}) = \frac{e^{-\beta F Y}}{\int dY\, d^N y\, e^{-\beta F Y}} \prod_i \Theta(Y - y_i) \quad \text{(A15)}$$

and integrating over all the y_i, one obtains

$$\rho_\beta(Y) = \frac{Y^N e^{-\beta F Y}}{\int dY\, Y^N e^{-\beta F Y}}. \quad \text{(A16)}$$

The mean value of this distribution is

$$\langle Y\rangle = \frac{k_B T(N+1)}{F}, \quad \text{(A17)}$$

whereas its variance is

$$\sigma_Y^2 = \frac{(N+1)(k_B T)^2}{F^2}. \quad \text{(A18)}$$

APPENDIX B

In this appendix we detail the derivation of the Langevin equation for the motion of the piston, following elementary kinetic theory. The basic idea is to estimate the average force exerted by the gas particles that collide with the piston, by calculating the average momentum exchanged in the collisions. The following approach dates back to Smoluchowski [26] and it has been used to write a Langevin equation for colloidal particles [27]. For the variable $y = Y - Y_{eq}$ we will derive a stochastic equation

$$M\frac{d^2 y}{dt^2} = F_{av}(y,\dot{y}) + C\eta, \quad \text{(B1)}$$

where $F_{av}(y,\dot{y})$ is the average force acting on the piston in the position $Y_{eq} + y$ and velocity $\dot{y}$, η is a white noise, and the constant C can be fixed *a posteriori* from the condition $M\langle\dot{y}^2\rangle = k_B T$.

Consider the gas at equilibrium and focus on the collision of the piston, characterized by its mass M and precollisional velocity V, and a particle of the gas, which is characterized by m and $\mathbf{v}$, respectively. The collision rule is

$$V' = V + \frac{2m}{m+M}(v_y - V), \quad v'_y = v_y - \frac{2M}{m+M}(v_y - V), \quad \text{(B2)}$$

where the primed quantity are postcollisional velocities and v_y is the y component of $\mathbf{v}$. The rate of such collisions can be obtained by considering the equivalent problem of a piston, at rest, hit by a flux of particles moving at relative velocity $V\hat{\mathbf{y}} - \mathbf{v}$. The rate is then determined by counting the number of pointlike particles hitting the unit surface in the infinitesimal time interval dt. This number corresponds to the particles contained in a rectangle of infinitesimal base length δx and height $(v_y - V)\Theta(v_y - V)dt$. The step function $\Theta(s)$ selects the condition for having a collision. Setting $v = v_y$, the mean force exerted by the particles of the gas on the piston is

$$\begin{aligned} F_{\text{coll}}(Y,V) &= \left\langle M\frac{\Delta V}{dt}\right\rangle \\ &= M\int_{-\infty}^{\infty} dv \int_0^L dx\, \rho(x,Y - r'_0) \\ &\quad \times \phi(v)(V' - V)(v - V)\Theta(v - V) \\ &= \frac{2mM}{m+M}\int_{-\infty}^{\infty} dv \int_0^L dx\, \rho(x,Y - r'_0) \\ &\quad \times \phi(v)\Theta(v - V)(v - V)^2, \end{aligned} \quad \text{(B3)}$$

where $\phi(v)$ is the equilibrium distribution of velocities of the gas, i.e.,

$$\phi(v) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv^2/2k_B T}, \quad \text{(B4)}$$

and $\rho(x,Y)$ is the spatial density of particles in the proximity of the piston. At equilibrium, this density is uniform on all the available volume and therefore depends on the position of the piston Y. Carrying on the integration on the spatial coordinates, we obtain

$$F_{\text{coll}}(Y,V) = \frac{2mM}{m+M}\lambda \int_V^{\infty} dv (v - V)^2 \phi(v), \quad \text{(B5)}$$

where $\lambda = \frac{N}{Y}$. We note that the equilibrium properties of the gas used in the derivation of this equation do not depend on the choice of the ensemble. Of course, $F_{av}(y,\dot{y})$ is nothing but $F_{\text{coll}} - F$.

In order to decouple the motion of the piston from the one of the gas molecules it is necessary to assume that $M \gg m$ and, moreover, that V is always small if compared to the thermal velocity of the particles $v_m = \sqrt{2k_B T/m}$: The expansion of the integral in Eq. (B5) in powers of $\sqrt{m/M}$ will give the viscous drag force appearing in the Langevin equation of motion. Defining $g = \sqrt{m/2k_B T}(v - V)$ and expanding perturbatively $\phi(v)$ as a function of g,

$$\begin{aligned} \exp\left(-\frac{m}{2k_B T}v^2\right) &= \exp\left[-\left(g + \sqrt{\frac{m}{2k_B T}}V\right)^2\right] \\ &\simeq \exp\left(-g^2 - \sqrt{\frac{2m}{k_B T}}gV\right) \\ &\simeq e^{-g^2}\left(1 - \sqrt{\frac{2m}{k_B T}}gV\right), \end{aligned} \quad \text{(B6)}$$

we can compute the integral, performing the change of variables $v \to g$,

$$\frac{2k_BT}{m\sqrt{\pi}}\int_0^\infty g^2e^{-g^2}\left(1-\sqrt{\frac{2m}{k_BT}}gV\right)dg=\frac{k_BT}{2m}-\sqrt{\frac{2k_BT}{\pi m}}V,$$

namely,

$$F_{\rm coll}=\frac{N}{Y}\left[\frac{M}{m+M}k_BT-2\frac{M}{m+M}\sqrt{\frac{2mk_BT}{\pi}}V\right].\quad\text{(B7)}$$

Expanding the previous expression to first order in y and V around the equilibrium position of the piston Y_{eq}, defined by the condition $F=F_{\rm coll}$ and $V=0$, we obtain a linear Langevin equation. The equilibrium conditions are

$$\frac{M}{m+M}k_BT\frac{N}{Y_{eq}}=F,\quad V_{eq}=0\quad\text{(B8)}$$

and therefore

$$Y_{eq}=\frac{NMk_BT}{F(m+M)}.\quad\text{(B9)}$$

The Langevin equation has the shape

$$\frac{d^2y}{dt^2}=-k_Ny-\gamma v+\frac{C}{M}\eta,\quad\text{(B10)}$$

where

$$\gamma=\frac{2F}{M}\sqrt{\frac{2m}{\pi k_BT}},\quad k_N=\frac{F^2(m+M)}{M^2Nk_BT}.\quad\text{(B11)}$$

It is easy to compute the correlation function

$$\langle V(t)V(0)\rangle=\frac{k_BT}{M}e^{-\gamma t/2}\left[\cosh\left(\frac{\Delta}{2}t\right)-\frac{\gamma}{\Delta}\sinh\left(\frac{\Delta}{2}t\right)\right],\quad\text{(B12)}$$

where $\Delta=\sqrt{\gamma^2-4k_N}$. Let us note that for any finite N (i.e., $k_N\neq 0$) one has $\int_0^\infty\langle V(t)V(0)\rangle dt=0$.

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