Single-particle distributions for small hard particle systems in the microcanonical and in the molecular-dynamics ensembles

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The exact results for the single-particle momentum distribution of a small system in the microcanonical ensemble [J.R. Ray and H.W. Graben, Phys Rev A **44**, 6905 (1991)] are extended to the case of the molecular-dynamics ensemble. Both cases are applied to systems with a reduced number of hard disks. Comparison with molecular-dynamics simulation illustrates the ergodicity of the studied systems.

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Very recently there has been a renewed interest in the statistical mechanics study of small systems in the microcanonical and in the molecular-dynamics ensembles. These studies may indeed have relevance in the field of clusters but also can give insight in other aspects related to the statistical mechanics of the problem. In this line recent work by Ackland [1] and Rouet and co-workers [2] address the issues of equipartition and ergodicity in closed one-dimensional hard-core systems. They analyze the velocity distribution, checking the differences between hard walls (microcanonical ensemble) and periodic boundaries (molecular-dynamics ensemble) which are of special importance for small systems. From a theoretical viewpoint, and obviating the problems of ergodicity, Ray and Graben [3] have studied the deviation from the Maxwell distribution for small systems in the microcanonical ensemble.

In this Brief Report the theoretical results by Ray and Graben [3] are compared with molecular-dynamics simulations. We also extend the theoretical results to the case of the molecular-dynamics ensemble in which the total momentum $\mathbf{M}$ of the system is conserved. In particular we shall restrict ourselves to hard disk systems. Indeed, although not very realistic, hard particle systems are close enough to the real systems studied in statistical mechanics. Besides, they have been shown to be both ergodic and mixing [4] for $N \geq 2$ spheres or disks, and this not only applies for systems enclosed in boxes with hard walls but also for periodic boundaries. For example, a system with two disks and periodic boundaries is equivalent to a Lorentz gas with a single point particle colliding with a periodic configuration of fixed scatterers, assumed to be disks. This model was also shown to be ergodic [5,6].

For the sake of completeness we shall start by briefly rederiving Ray and Graben results for the microcanonical ensemble. This is the appropriate ensemble for a hard particle system with hard bounds. Notice that in this case the particle collisions conserve kinetic energy and momentum but the collisions with the walls only preserve the kinetic energy. The probability distribution for the momentum $\mathbf{p}_a$ of particle a is given by [3]

$$\omega_M(\mathbf{p}_a) = \frac{1}{\Omega(E)} \int d^{fN}\mathbf{q}\, d^{f(N-1)}\mathbf{p}\, \delta(E - H(\mathbf{q},\mathbf{p})), \tag{1}$$

where the label M in ω_M stands for microcanonical, N is the number of particles, f is the dimensionality of the space, E is the total energy of the system, $H(\mathbf{q},\mathbf{p})$ is the Hamiltonian of the system, and $(\mathbf{q},\mathbf{p}) \equiv (\mathbf{q}_1,\ldots,\mathbf{q}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)$ where $(\mathbf{q}_i,\mathbf{p}_i)$ denotes position and momentum of particle i. Finally, $\Omega(E)$ is a normalization factor: the density of states,

$$\Omega(E) = \int d^{fN}\mathbf{q}\, d^{fN}\mathbf{p}\, \delta(E - H(\mathbf{q},\mathbf{p})). \tag{2}$$

We shall assume that the Hamiltonian can be written as $H = K(p) + U(q)$, where K is the kinetic energy of the N-particle system, depending only on the momentum coordinates, and U is the potential energy, supposed to depend only on the position coordinates. We shall also assume the usual functional form for the kinetic energy

$$K(p) = \sum_{i=1}^{N} K_i(\mathbf{p}_i) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^{\,2}}{2m_i}, \tag{3}$$

where m_i is the mass of particle i.

In order to obtain a simple analytical expression for $\omega_M(\mathbf{p}_a)$ we notice that Eq. (1) can be written as

$$\omega_M(\mathbf{p}_a) = \frac{1}{\Omega(E)} \int d^{fN}\mathbf{q}\, I(\mathbf{p}_a,\mathbf{q},E), \tag{4}$$

where

$$I(\mathbf{p}_a,\mathbf{q},E) = \int d^{f(N-1)}\mathbf{p}\, \delta(E - H). \tag{5}$$

The integration with respect to the momentum coordinates in (5) can be carried out by means of the Laplace transform of the δ function. A subsequent inverse Laplace transform yields

$$I(\mathbf{p}_a,\mathbf{q},E) = \frac{\prod_{j\neq a}^{N}(2\pi m_j)^{f/2}}{\Gamma(f(N-1)/2)} \hat{E}^{f(N-1)/2-1}\Theta(\hat{E}), \tag{6}$$

where Γ is the gamma Euler function, Θ is the Heaviside step function, and $\hat{E} = E - U(\mathbf{q}) - K_a(\mathbf{p}_a)$.

The integration over momenta in $\Omega(E)$ [see Eq. (2)] can be performed in a similar way obtaining

$$\Omega(E) = \int d^{fN}\mathbf{q}\ \frac{\prod_{j=1}^{N}(2\pi m_j)^{f/2}}{\Gamma(fN/2)} E'^{fN/2-1}\Theta(E'), \quad (7)$$

where now $E' = E - U(\mathbf{q})$. Finally, from (4), (6), and (7) we get the following result for the single-particle momentum distribution in the microcanonical ensemble [3]:

$$\omega_M(\mathbf{p}_a) = \frac{\Gamma(fN/2)}{(2m_a\pi)^{f/2}\Gamma(f(N-1)/2)} \frac{\int d^{fN}\mathbf{q}\ \left[E - \frac{\mathbf{p}_a^2}{2m_a} - U(\mathbf{q})\right]^{f(N-1)/2-1} \Theta\left(E - \frac{\mathbf{p}_a^2}{2m_a} - U(\mathbf{q})\right)}{\int d^{fN}\mathbf{q}\ [E - U(\mathbf{q})]^{f(N-1)/2-1}\Theta(E - U(\mathbf{q}))}. \quad (8)$$

If we consider hard particles, the integrands in (8) are nonvanishing only when $U(\mathbf{q}) = 0$; in this case the terms $\left(E - \mathbf{p}_a^2/2m_a\right)^{f(N-1)/2-1}$ and $E^{fN/2-1}$ can be taken out of the corresponding integrals and, therefore, equivalent integrals remain in the denominator and in the numerator, which obviously cancel. This fact gives us the following expression for the momentum distribution of one individual hard particle in the microcanonical ensemble [3]:

$$\omega_M(\mathbf{p}_a) = \frac{\Gamma(fN/2)}{(2m_a\pi E)^{f/2}\Gamma(f(N-1)/2)} \times \left[1 - \frac{\mathbf{p}_a^2}{2m_a E}\right]^{f(N-1)/2-1} \Theta\left(1 - \frac{\mathbf{p}_a^2}{2m_a E}\right). \quad (9)$$

Notice that this result was also obtained in [1,2] for hard rods and coincides with the microcanonical distribution for an ideal gas [7] . A further integration over the angular variables yields the distribution of momentum moduli

$$\omega_M(p_a) = \frac{2\pi^{f/2}}{\Gamma(f/2)} p_a^{f-1} \frac{\Gamma(fN/2)}{(2\pi m_a E)^{f/2}\Gamma(f(N-1)/2)} \times \left(1 - \frac{p_a^2}{2m_a E}\right)^{f(N-1)/2-1} \Theta\left[1 - \frac{p_a^2}{2m_a E}\right] \quad (10)$$

and, for the particular case of hard disks ($f = 2$) one has

$$\omega_M(\mathbf{p}_a) = \frac{N-1}{2\pi m_a E}\left[1 - \frac{\mathbf{p}_a^2}{2m_a E}\right]^{N-2} \Theta\left[1 - \frac{\mathbf{p}_a^2}{2m_a E}\right] \quad (11)$$

and

$$\omega_M(p_a) = \frac{(N-1)p_a}{m_a E}\left[1 - \frac{{p_a}^2}{2m_a E}\right]^{N-2} \Theta\left[1 - \frac{p_a^2}{2m_a E}\right] \quad (12)$$

for the momentum distribution and the momentum moduli distribution, respectively.

A usual procedure in molecular dynamics is to consider periodic boundary conditions to dismiss the surface effects due to considering a finite system. When a particle crosses a cell bound there is not momentum change as it happens when a particle reaches a hard bound. For the case of an isolated system with elastic particle collisions, besides the energy E, number of particles N, and volume V conservation proper of the microcanonical ensemble, the total momentum $\mathbf{M}$ of the system is also conserved and this new constraint must be taken into account. This special case of the microcanonical ensemble is the so-called molecular-dynamics ensemble [8].

The natural extension of the microcanonical density function to the molecular-dynamics case is given by

$$\rho_{\mathrm{MD}}(\mathbf{q},\mathbf{p}) = \frac{1}{\Omega_{\mathrm{MD}}(E,\mathbf{M})}\ \delta(E - H(\mathbf{q},\mathbf{p}))\ \delta(\mathbf{M} - \mathbf{P}), \quad (13)$$

where the label MD stands for molecular-dynamics, $\mathbf{M}$ is the total linear momentum of the system,

$$\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i, \quad (14)$$

$$\delta(\mathbf{M} - \mathbf{P}) = \prod_{\alpha=1}^{f} \delta(M_\alpha - P_\alpha), \quad (15)$$

and

$$\Omega_{\mathrm{MD}}(E,\mathbf{M}) = \int d^{fN}\mathbf{q}\ d^{fN}\mathbf{p}\ \delta(E - H(\mathbf{q},\mathbf{p})) \times \delta(\mathbf{M} - \mathbf{P}). \quad (16)$$

The one particle momentum distribution is obtained by integrating over all the coordinates except $\mathbf{p}_a$:

$$\omega_{\mathrm{MD}}(\mathbf{p}_a) = \frac{1}{\Omega_{\mathrm{MD}}(E,\mathbf{M})} \int d^{fN}\mathbf{q}\ d^{f(N-1)}\mathbf{p} \times \delta(E - H(\mathbf{q},\mathbf{p}))\delta(\mathbf{M} - \mathbf{P}). \quad (17)$$

Notice that this expression is completely analogous to (1) and therefore can be evaluated in a similar way by considering the Laplace representation of $\delta(E - H(\mathbf{q},\mathbf{p}))$ and the Fourier representation of $\delta(\mathbf{M} - \mathbf{P})$ so that the momentum integrals can be performed in Eq. (16). The subsequent inverse Fourier and Laplace transform can be carried out to yield

$$\omega_{\mathrm{MD}}(\mathbf{p}_a) = \{[\Gamma(f(N-1)/2)]/[(2\pi m_a)^{f/2}\Gamma(f(N-2)/2)]\} \left[\sum_{j=1}^{N} m_j \Big/ \left(\sum_{j=1}^{N} m_j - m_a\right)\right]^{f/2} \times \frac{\int d^{fN}q\ \left(E - \frac{{\mathbf{p}_a}^2}{2m_a} - \frac{(\mathbf{M}-\mathbf{p}_a)^2}{2\sum_{j\neq a}^{N} m_j} - U(\mathbf{q})\right)^{f(N-2)/2-1} \Theta\left(E - \frac{{\mathbf{p}_a}^2}{2m_a} - \frac{(\mathbf{M}-\mathbf{p}_a)^2}{2\sum_{j\neq a}^{N} m_j} - U(\mathbf{q})\right)}{\int d^{fN}\mathbf{q}\ \left(E - \frac{\mathbf{M}^2}{2\sum_{j=1}^{N} m_j} - U(\mathbf{q})\right)^{f(N-1)/2-1} \Theta\left(E - \frac{\mathbf{M}^2}{2\sum_{j=1}^{N} m_j} - U(\mathbf{q})\right)}. \quad (18)$$

Again, for hard particles the integrands in (18) are nonzero only when $U(\mathbf{q}) = 0$. In that case the integrals in the numerator and in the denominator are identical and, therefore, cancel out. The final result is

$$\omega_{\mathrm{MD}}(\mathbf{p}_a) = \{[\Gamma(f(N-1)/2)]/[(2\pi m_a)^{f/2}\Gamma(f(N-2)/2)]\}\left[\sum_{j=1}^{N} m_j \Big/ \left(\sum_{j=1}^{N} m_j - m_a\right)\right]^{f/2} \times \frac{\left(E - \frac{\mathbf{p}_a{}^2}{2m_a} - \frac{(\mathbf{M}-\mathbf{p}_a)^2}{2\sum_{j\neq a}^{N} m_j}\right)^{f(N-2)/2-1}}{\left(E - \frac{\mathbf{M}^2}{2\sum_{j=1}^{N} m_j}\right)^{f(N-1)/2-1}} \Theta\left(E - \frac{\mathbf{p}_a{}^2}{2m_a} - \frac{(\mathbf{M}-\mathbf{p}_a)^2}{2\sum_{j\neq a}^{N} m_j}\right). \tag{19}$$

For $\mathbf{M} = \mathbf{0}$ (the usual case in molecular-dynamics calculations), it is possible to obtain from (19) an analytical expression for the distribution of momentum moduli:

$$\omega_{\mathrm{MD}}(p_a) = A p_a^{f-1}\left(\frac{S}{S_a}\right)^{f/2}\left(1 - \frac{S p_a^2}{2m_a E S_a}\right)^{f(N-2)/2-1} \times \Theta[1 - (S p_a^2/2m_a E S_a)], \tag{20}$$

where

$$A = \frac{2\Gamma(f(N-1)/2)}{(2m_a E)^{f/2}\Gamma(f(N-2)/2)\Gamma(f/2)}, \tag{21}$$

$$S = \sum_{j=1}^{N} m_j, \tag{22}$$

$$S_a = \sum_{j\neq a} m_j. \tag{23}$$

Particularizing (19) for particles with equal masses (i.e., $m_i = m$) and dimension $f = 2$ we get

$$\omega_{\mathrm{MD}}(\mathbf{p}) = \frac{N(N-2)}{(N-1)2\pi m}\frac{\left(E - \frac{(\mathbf{M}-\mathbf{p})^2}{2m(N-1)} - \frac{\mathbf{p}^2}{2m}\right)^{N-3}}{\left(E - \frac{\mathbf{M}^2}{2mN}\right)^{N-2}} \times \Theta\left(E - \frac{(\mathbf{M}-\mathbf{p})^2}{2m(N-1)} - \frac{\mathbf{p}^2}{2m}\right), \tag{24}$$

and for $\mathbf{M} = \mathbf{0}$, distribution (20) takes the form

$$\omega_{\mathrm{MD}}(p) = \frac{N(N-2)p}{(N-1)mE^{N-2}}\left[E - \frac{Np^2}{2m(N-1)}\right]^{N-3} \times \Theta(E - \{Np^2/[2m(N-1)]\}). \tag{25}$$

Notice that these expressions are only valid for $N \geq 3$. For $N = 2$ one has

$$\omega_{\mathrm{MD}}(\mathbf{p}) = (1/m\pi)\ \delta(E - \{[(\mathbf{M}-\mathbf{p})^2 + \mathbf{p}^2]/2m\}) \tag{26}$$

and again, for $\mathbf{M} = \mathbf{0}$, the distribution of momentum moduli is

$$\omega_{\mathrm{MD}}(p) = (2p/m)\ \delta[E - (p^2/m)], \tag{27}$$

as one could expect.

Until now we have presented the exact theoretical results for the momentum distributions of the two considered systems obtained in the framework of the ensemble method of Gibbs. The functional form of the density function is thus a direct consequence of Tolman's principle of equal *a priori* probabilities. Since we are considering ergodic systems, these Gibbs statistical mechanics results (based on phase averages) must coincide with results coming from a time average based statistical mechanics (*à la* Boltzmann), providing therefore a further numerical evidence of the ergodicity of the system.

In what follows we shall present the results obtained from molecular-dynamics calculations and their comparison with the above theoretical results. In the simulations we have considered some cases in both the microcanonical and the molecular-dynamics ensembles for systems with a very reduced number of particles ($N = 2, 3, 4, 5, \ldots$). Referring to the methodology of calculations, all simulations in the present work were performed by using the standard technique for simulating hard particle systems [9]. Also, concerning the assumptions in the simulations and the presentation of results, we must make the following remarks:

(1) We assume hard disks ($f = 2$) with equal radius and mass. Notice that taking mixtures of disks with different masses or radii would give the same results for the momentum distribution.

(2) For the sake of simplicity all the quantities considered are expressed in units of E, m, and R. We also take $E = 1$, $m = 1$, and $R = 1$ in all the simulations.

(3) The temperature is not a relevant parameter in a hard particle system.

(4) The density of the system does not affect the functional form of the momentum distribution, it only modifies the collision frequency.

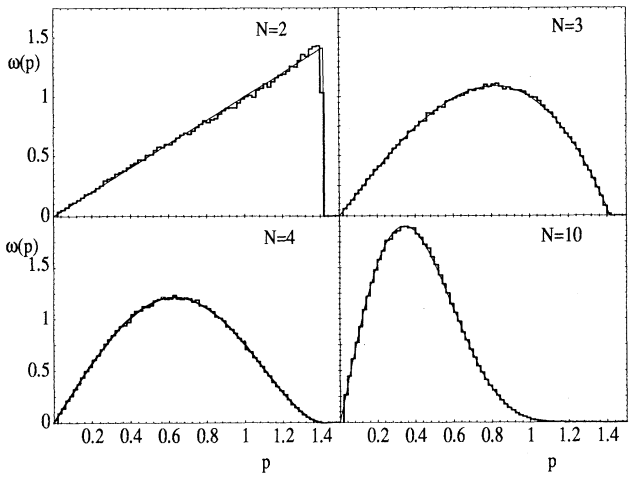

FIG. 1. Distribution of moment moduli in the microcanonical ensemble. Thin line: theoretical result (12). Thick line: simulation result. Total energy of the system $E = 1$.

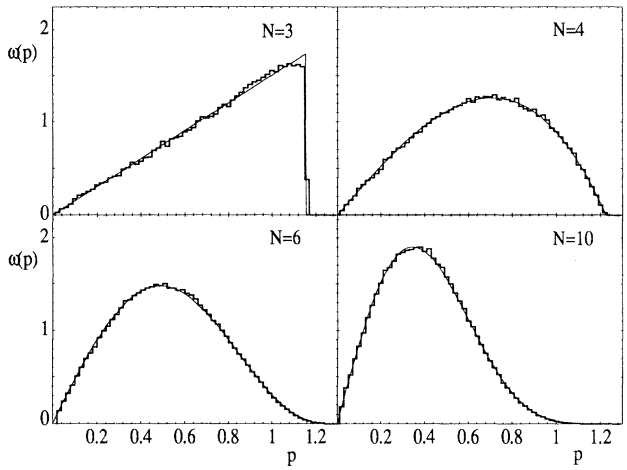

FIG. 2. Distribution of moment moduli in the molecular-dynamics ensemble. Thin line: theoretical result (25). Thick line: simulation result. Total momentum of the system $\boldsymbol{M} = (0,0)$. Total energy of the system $E = 1$.

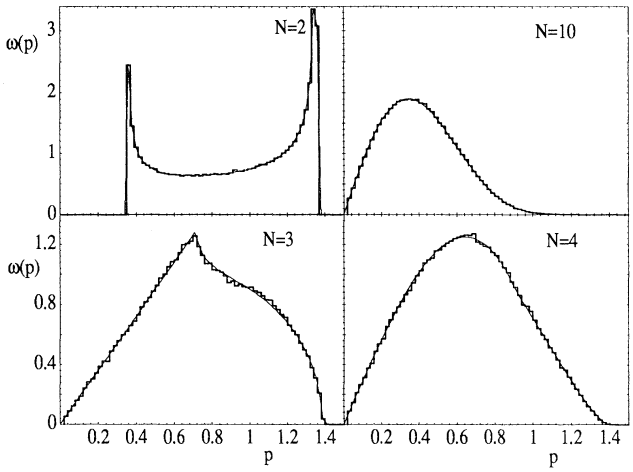

FIG. 3. Same as Fig. 2 except that $\boldsymbol{M} = (1,0)$.

(5) For systems with periodic boundary conditions we consider the cases $\mathbf{M} = (0,0)$ and $\mathbf{M} = (1,0)$ in the above units.

(6) In order to get reasonable statistics we have considered runs with 2×10^5 collisions per particle in the average. We gathered data every N collisions.

(7) The results of the simulations are presented in histograms with bins of a length of 0.02 moment units. In order to compare with these histograms, the theoretical results have been discretised in bins of equal length.

In Fig. 1 we have plotted the microcanonical results corresponding to $N = 2$, 3, 4, and 10 particles. The agreement between theoretical and simulation results is excellent even in the case of two particles.

Figure 2 corresponds to systems with periodic boundary conditions and total momentum $\mathbf{M} = (0,0)$. For the case $N = 2$, and because the total momentum is zero, both particle momenta coincide in modulus and direction (with opposite sense), so that at the point $p = \sqrt{mE}$ one obtains a Dirac delta distribution [see Eqs. (26) and (27)]. For other cases ($N = 3$, 4, 6, and 10) an excellent agreement with the theoretical expressions is also observed.

Finally, in Fig. 3 one observes the effect of taking $\mathbf{M} \neq (0,0)$ (i.e., when the system has a collective motion). In this figure we present results for the cases $N = 2$, 3, 4, and 10. Notice also the very good agreement between the simulation results and those obtained from numerical integration of Eqs. (26) and (24) over the angular variables.

To summarize, in this Brief Report we have calculated theoretically and by simulation the single-particle momentum distributions for small hard particle systems in the microcanonical and in the molecular-dynamics ensembles. The mathematical proof of the ergodicity of the considered systems is not a trivial task. In this context we have given a numerical verification of the ergodicity of these systems by comparing theoretic (phase average based) and simulation (time average based) results.

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