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Microcanonical ensemble study of a classical fluid of hard rods under gravity

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Abstract. The study of a system of hard rods in a box of finite length in the presence of a uniform gravitational field is made by means of the microcanonical ensemble. Explicit expressions are derived for the phase volume and the density of states, the primary functions of this ensemble. Related statistical quantities are reported, such as the entropy, the temperature, the heat capacity and the forces exerted on the fluid by the bottom and top walls. The microcanonical number density and higher order molecular distribution functions are also derived.

PACS. 05.20.Gg Classical ensemble theory

1 Introduction

One-dimensional systems often provide exactly solvable models which might serve as guides to higher dimensional problems. In particular, the hard-rod system has proved to be very useful in the study of the structure of inhomogeneous fluids. This is the case of a system of hard rods under gravity which can be useful, for example, in the analysis of equilibrium sedimentation profiles of colloidal suspensions in a gravitational field [1].

A semi-infinite system of hard rods confined to the region $z > 0$ by a hard wall at $z = 0$ in the presence of an arbitrary external field was reported by Percus [2], who obtained an equation for the density profile of hard rods in the grand canonical ensemble. A finite system, in which the hard rods are confined in a box of finite length in the presence of a uniform gravitational field, has been very recently reported by Ibsen *et al.* [3]. These authors obtained explicit expressions, in the canonical ensemble, for the forces exerted on the fluid by the bottom and top walls and, both in the canonical and in the grand canonical ensembles, for the number density and higher order molecular distribution functions.

In the present work we consider the microcanonical ensemble study of a finite system of hard rods in a gravitational field. Nowadays it has been recognized the interest of applying the microcanonical method to specific systems. Some possible reasons of this interest are the following. First, the study of *ensemble differences* between microcanonical and canonical expressions and their equivalence in the thermodynamic limit. Second, the fact that many computer simulations have been designed for finite systems having a constant total energy [4], and thus requiring the microcanonical expressions for a correct interpretation of the computer results. Third, the necessity of developing practical analytical methods to work out in the microcanonical ensemble which can be applied to new problems as they arise.

The structure of the paper is as follows. Section 2 is devoted to the calculation of the phase volume and the density of states for the system under consideration. These expressions are used in Section 3 for calculating the entropy, the temperature, the forces exerted on the fluid by the bottom and top walls, and the heat capacity of the system in the microcanonical ensemble. In Section 4, explicit expressions for the microcanonical molecular distribution functions are derived, and the main features of the number density profile are analyzed. We compare numerically the expressions obtained both for the forces exerted by the walls and for the number density with the canonical ones reported by Ibsen *et al.* [3]. Some conclusions are summarized in Section 5. This paper follows closely the ideas presented in reference [5] for an ideal gas under the influence of a gravitational field in the microcanonical ensemble.

2 Microcanonical ensemble

We consider a system of N hard rods of mass m and length σ in a linear box of length L in the presence of a uniform gravitational field of strength g. The Hamiltonian of the system takes the form:

$$\mathcal{H}(\mathbf{z}_N, \mathbf{p}_N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(\mathbf{z}_N; z_0, z_{N+1}) \qquad (1)$$

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where $(\mathbf{z}_N, \mathbf{p}_N) \equiv (z_1, ..., z_N; p_1, ..., p_N)$ denote the position of the centers and the momentum of the hard rods and the total potential energy is given by

$$U(\mathbf{z}_N; z_0, z_{N+1}) = \sum_{i<j} u(|z_j - z_i|) + \sum_{i=1}^{N} mgz_i + \sum_{i=1}^{N} U_w(z_i; z_0, z_{N+1}), \tag{2}$$

where

$$u(|z_j - z_i|) = \begin{cases} \infty, & |z_j - z_i| < \sigma \\ 0, & |z_j - z_i| \geq \sigma \end{cases} \tag{3}$$

is the interparticle pair potential, and

$$U_w(z_i; z_0, z_{N+1}) = \begin{cases} 0, & z_0 + \sigma \leq z_i \leq z_{N+1} - \sigma \\ \infty, & \text{otherwise} \end{cases} \tag{4}$$

is the potential due to the bottom and top walls of the box and where z_0 and z_{N+1} are the positions of the centers of fixed hard rods that define the bottom wall and the top wall, respectively, so that $z_{N+1} - z_0 = L + \sigma$. The positions of the hard rods verify: $z_1 < ... < z_N$ and $z_N - z_1 \leq L - \sigma$.

Assuming that the macrostate of the system is defined by a constant energy E, a fixed length L, and a fixed number of particles N, its statistical thermodynamic study must be made in the microcanonical ensemble framework. The primary functions of this ensemble are the *phase volume*, $\Phi(E, L, N)$, and the *density of states*, $\Omega(E, L, N)$, defined by

$$\Phi(E, L, N) = \frac{1}{h^N} \int ... \int \Theta\left[E - \mathcal{H}(\mathbf{z}_N, \mathbf{p}_N)\right] d\mathbf{z}_N d\mathbf{p}_N, \tag{5}$$

$$\Omega(E, L, N) = \frac{1}{h^N} \int ... \int \delta\left[E - \mathcal{H}(\mathbf{z}_N, \mathbf{p}_N)\right] d\mathbf{z}_N d\mathbf{p}_N = \left(\frac{\partial \Phi(E, L, N)}{\partial E}\right)_{L,N}, \tag{6}$$

where $d\mathbf{z}_N d\mathbf{p}_N \equiv dz_1 ... dz_N dp_1 ... dp_N$, h is the Planck constant, $\Theta(x)$ is the Heaviside step function and $\delta(x)$ is the Dirac delta function. The microcanonical average of any dynamical function $A(\mathbf{z}_N, \mathbf{p}_N)$ is obtained from

$$\langle A \rangle = \frac{1}{h^N \Omega(E, L, N)} \iint A(\mathbf{z}_N, \mathbf{p}_N) \times \delta\left[E - \mathcal{H}(\mathbf{z}_N, \mathbf{p}_N)\right] d\mathbf{z}_N d\mathbf{p}_N. \tag{7}$$

Taking into account the Hamiltonian (1) and introducing variables $x_k = z_k - (z_0 + k\sigma)$, integration over momenta in (5) gives

$$\Phi(E, L, N) = \frac{(2\pi m)^{N/2}}{h^N \Gamma\left(\frac{N}{2} + 1\right)} \int_0^{\bar{L}} dx_N \times \int_0^{x_N} dx_{N-1} ... \int_0^{x_2} dx_1 \left(E - mg\alpha - mg \sum_{i=1}^{N} x_i\right)^{N/2} \times \Theta\left(E - mg\alpha - mg \sum_{i=1}^{N} x_i\right), \tag{8}$$

where $\Gamma(x)$ is the Euler gamma function and

$$\alpha = Nz_0 + \frac{N(N+1)}{2}\sigma, \tag{9}$$

$$\bar{L} \equiv x_{N+1} = z_{N+1} - z_0 - (N+1)\sigma = L - N\sigma. \tag{10}$$

The integrals in (8) can be evaluated by using the Laplace-transform technique [5,6]. A straightforward calculation leads to

$$\Phi(E, L, N) \equiv \Phi(z_0, z_{N+1}; N) = \frac{(2\pi m)^{\frac{N}{2}}}{h^N (mg)^N \Gamma(N+1) \Gamma(\frac{3N}{2} + 1)} \times \phi_N(E - mg\alpha, mg\bar{L}, 0, 0), \tag{11}$$

where we have defined

$$\phi_N(a, b, n, \nu) \equiv \sum_{k=0}^{N} (-1)^k \binom{N}{k} k^n (a - kb)^{\frac{3N}{2} - \nu} \Theta(a - kb) \Theta(b). \tag{12}$$

We note the dependence of the phase volume (11) on z_0 and z_{N+1} through the parameters α and $\bar{L}$ given by equations (9, 10), respectively.

From equations (6, 11), we obtain

$$\Omega(E, L, N) \equiv \Omega(z_0, z_{N+1}; N) = \frac{(2\pi m)^{\frac{N}{2}}}{h^N (mg)^N \Gamma(N+1) \Gamma(\frac{3N}{2})} \times \phi_N(E - mg\alpha, mg\bar{L}, 0, 1), \tag{13}$$

for the density of states. In the case of a column of infinite height, $L \to \infty$, expression (13) leads to

$$\Omega(E, N) = \frac{(2\pi m)^{N/2}}{h^N (mg)^N \Gamma(N+1) \Gamma\left(\frac{3N}{2}\right)} \times (E - mg\alpha)^{\frac{3N}{2} - 1} \Theta(E - mg\alpha). \tag{14}$$

This expression is also valid for systems with finite height but with energies small enough so that $E - mg\alpha \leq mg\bar{L}$. In this case the hard rods never reach the top wall and the system becomes L-independent. This is a characteristic of the microcanonical ensemble study.

3 Thermodynamic study

3.1 Entropy, temperature and heat capacity

In the microcanonical ensemble there are several definitions for the entropy. One of them, based on both the theorem of adiabatic invariance of phase volume and on the fact that it yields exactly the equipartition theorem [6], is

$$S(E, L, N) = k_B \ln \Phi(E, L, N)\,. \tag{15}$$

We will take the entropy definition (15) for deriving all equations reported in this section. From equations (11, 15) one then obtains,

$$S(E, L, N) = S_0(E, L, N) + S_{exc}(E, L, N)\,, \tag{16}$$

where

$$S_0(E, L, N) = k_B \ln \left[\frac{(L - N\sigma)^N (2\pi m E)^{N/2}}{h^N \Gamma(N+1) \Gamma\left(\frac{N}{2}+1\right)} \right], \tag{17}$$

is the microcanonical entropy of the system of hard rods in absence of gravity, and

$$\begin{aligned} S_{exc}(E, L, N) &\equiv S_{exc}(y, N) \\ &= k_B \ln \left[\frac{\Gamma\left(\frac{N}{2}+1\right)}{\Gamma\left(\frac{3N}{2}+1\right)} \frac{(E - mg\alpha)^{\frac{N}{2}}}{E^{\frac{N}{2}}} \frac{\phi_N(1, y, 0, 0)}{y^N} \right], \end{aligned} \tag{18}$$

is the excess entropy due to the presence of a uniform gravitational field, and where

$$y = \frac{mg\bar{L}}{E - mg\alpha} = \frac{\bar{\ell}}{\sigma_g}\,, \tag{19}$$

with

$$\bar{\ell} = \frac{\bar{L}}{N} = \frac{L}{N} - \sigma\,, \tag{20}$$

and

$$\sigma_g = \frac{E - mg\alpha}{Nmg}\,, \tag{21}$$

being characteristic lengths of the system. From expression (18) one can make an analysis of the ordering effect of the gravitational field, similar to the one reported in reference [5] for the ideal gas case (see also [7,8]).

In the microcanonical ensemble, the statistical temperature of the system is defined by

$$\frac{1}{k_B T} = \frac{1}{k_B} \left(\frac{\partial S}{\partial E} \right)_{L,N} = \left(\frac{\partial \ln \Phi}{\partial E} \right)_{L,N} = \frac{\Omega}{\Phi}\,. \tag{22}$$

From equations (11, 13), one easily obtains

$$\begin{aligned} k_B T &= \frac{2}{3N} \frac{\phi_N(E - mg\alpha, mg\bar{L}, 0, 0)}{\phi_N(E - mg\alpha, mg\bar{L}, 0, 1)} \\ &= \frac{2(E - mg\alpha)}{3N} \frac{\phi_N(1, y, 0, 0)}{\phi_N(1, y, 0, 1)}\,. \end{aligned} \tag{23}$$

Equation (23) shows that a hard-rod fluid has the same microcanonical temperature than a one-dimensional ideal gas with energy $E' = E - mg\alpha$ in a box of length $\bar{L}$ [5].

Taking into account equations (6, 22), in the microcanonical ensemble the heat capacity C_L at constant L and N can be obtained in terms of the density of states $\Omega(E, L, N)$,

$$C_L = \left(\frac{\partial T}{\partial E} \right)_{L,N}^{-1} = N k_B \left[N - N k_B T \left(\frac{\partial \ln \Omega}{\partial E} \right)_{L,N} \right]^{-1}. \tag{24}$$

From equations (13, 23, 24) one obtains

$$\frac{C_L}{N k_B} = \left[N - \left(\frac{3N-2}{3} \right) \frac{\phi_N(1, y, 0, 0) \phi_N(1, y, 0, 2)}{\phi_N^2(1, y, 0, 1)} \right]^{-1}, \tag{25}$$

with $\phi_N(a, b, n, \nu)$ given by (12). Expression (25) is identical to the one obtained for the ideal gas case with energy $E' = E - mg\alpha$ in a box of length $\bar{L}$ [5].

3.2 Forces exerted by the walls of the box

The force exerted on the fluid by the bottom and top walls can be obtained by deriving the entropy w.r.t. the positions of the walls z_0 and z_{N+1}, respectively. From equations (11), and taking into account equations (9, 10), one obtains:

$$\begin{aligned} \frac{F_b}{k_B T} &= -\frac{1}{k_B} \frac{\partial S}{\partial z_0} = -\frac{\partial \ln \Phi}{\partial z_0} \\ &= mg \frac{3N}{2} \left[\frac{N \phi_N(E - mg\alpha, mg\bar{L}, 0, 1)}{\phi_N(E - mg\alpha, mg\bar{L}, 0, 0)} \right. \\ &\quad \left. - \frac{\phi_N(E - mg\alpha, mg\bar{L}, 1, 1)}{\phi_N(E - mg\alpha, mg\bar{L}, 0, 0)} \right], \end{aligned} \tag{26}$$

$$\begin{aligned} \frac{F_t}{k_B T} &= \frac{1}{k_B} \frac{\partial S}{\partial z_{N+1}} = \frac{\partial \ln \Phi}{\partial z_{N+1}} \\ &= -mg \frac{3N}{2} \frac{\phi_N(E - mg\alpha, mg\bar{L}, 1, 1)}{\phi_N(E - mg\alpha, mg\bar{L}, 0, 0)}\,. \end{aligned} \tag{27}$$

From these equations and using (23), one obtains:

$$F_b = mgN \left[1 - \frac{1}{N} \frac{\phi_N(1, y, 1, 1)}{\phi_N(1, y, 0, 1)} \right], \tag{28}$$

$$F_t = -mg \frac{\phi_N(1, y, 1, 1)}{\phi_N(1, y, 0, 1)}\,. \tag{29}$$

One can see that $F_b - F_t = mgN$, *i.e.*, the weight of the system and thus mechanical equilibrium is fulfilled. From equations (26, 27) one easily obtains the two expected limit results

$$F_b = F_t = \frac{2E}{\bar{L}} = \frac{N k_B T}{L - N\sigma} \qquad \text{for } g \to 0\,, \tag{30}$$

$$n(z) = \frac{(2\pi m)^{N/2}}{h^N (mg)^{N-1} \Gamma\left(\frac{3N}{2}-1\right) \Omega(z_0, z_{N+1}; N)} \sum_{j=1}^{N} \frac{1}{\Gamma(j)\Gamma(N-j+1)} \sum_{j_1=0}^{j-1} \sum_{j_2=0}^{N-j} (-1)^{j_1+j_2} \binom{j-1}{j_1} \binom{N-j}{j_2}$$
$$\times \left[E - mgz - mgb_j - j_1 mg\xi_j - j_2 mg(\bar{L} - \xi_j)\right]^{\frac{3N}{2}-2}$$
$$\times \Theta\left[E - mgz - mgb_j - j_1 mg\xi_j - j_2 mg(\bar{L} - \xi_j)\right] \Theta(\xi_j)\Theta(\bar{L} - \xi_j), \quad (36)$$

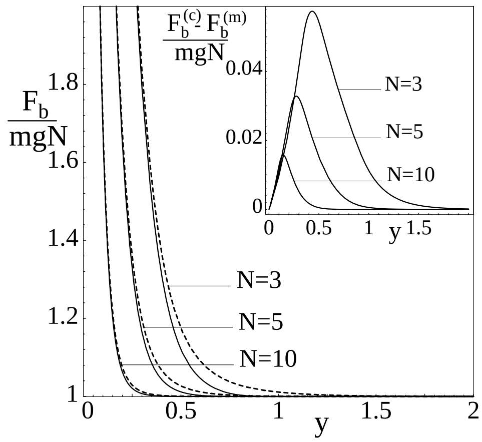

Fig. 1. Microcanonical (solid lines) and canonical (dashed lines) reduced force F_b/mgN as a function of $y = \bar{\ell}/\sigma_g$, for $N = 3, 5$ and 10. Microcanonical curves have been obtained from (28), while canonical curves have been obtained from expression (8) of reference [3] and (23). The inset shows the difference between canonical (c) and microcanonical (m) results.

$$F_b = mgN \quad F_t = 0 \quad \text{for } y \geq 1 \quad (E - mg\alpha \leq mg\bar{L}). \quad (31)$$

Figure 1 shows the microcanonical (solid lines) dimensionless force F_b/Nmg as a function of y for different values of N. We can see that at given N, F_b/Nmg decreases as y increases (larger g, larger $\bar{L}$ and/or smaller $E - mg\alpha$). In this figure the corresponding canonical dimensionless force obtained by substituting k_BT/mg given by (23) in the expression reported by Ibsen *et al.* [3] is also plotted (dashed lines). The difference between canonical and microcanonical forces is shown in the inset of Figure 1. We can see that microcanonical results approach the canonical ones very quickly as N increases.

4 Microcanonical molecular distribution functions

The number density of hard rods at a given height z can be derived from its definition as an ensemble average:

$$n(z) = \left\langle \sum_{j=1}^{N} \delta(z_j - z) \right\rangle . \quad (32)$$

By using (7), we can write

$$\langle \delta(z_j - z) \rangle = \frac{\Omega_j(E - mgz; z)}{h^N \Omega(z_0, z_{N+1}; N)}, \quad (33)$$

where $\Omega(z_0, z_{N+1}; N)$ is given by (13), and

$$\Omega_j(E - mgz; z) = \frac{\partial \Phi_j(E - mgz; z)}{\partial E} \cdot \quad (34)$$

with

$$\Phi_j(E - mgz; z) = \int ... \int \Theta\Big[E - \sum_{i=1}^{N} \frac{p_i^2}{2m}$$
$$- U(z_1, ..., z_{j-1}; z_0, z) - U(z_{j+1}, ..., z_N; z, z_{N+1})\Big]$$
$$\times\, dz_1 ... dz_{j-1} dz_{j+1} ... dz_N dp_1 ... dp_N \,, \quad (35)$$

where $U(z_1, ..., z_{j-1}; z_0, z)$ and $U(z_{j+1}, ..., z_N; z, z_{N+1})$ are given by (2). This function can be evaluated following a procedure similar to the one used for the phase volume (8). Substituting Φ_j into (34), and using equations (32, 33), we obtain

see equation (36) above

for the microcanonical number density for a finite system of hard rods under gravity, where

$$b_j = (j-1)z_0 + (N-j)z + \frac{(j-1)j}{2}\sigma + \frac{(N-j)(N-j+1)}{2}\sigma \,, \quad (37)$$

$$\xi_j = z - z_0 - j\sigma \,. \quad (38)$$

In the limit $(g \to 0)$, expression (36) becomes:

$$n_0(z) = \frac{N}{\bar{L}^N} \sum_{j=1}^{N} \binom{N-1}{j-1} \xi_j^{j-1} (\bar{L} - \xi_j)^{N-j} \Theta(\xi_j)\Theta(\bar{L} - \xi_j) \,, \quad (39)$$

which gives the number density reported by Leff *et al.* [9] using the canonical ensemble for a system of hard rods in a box of finite length in absence of gravity.

The shape of the microcanonical number density (36) is governed by the characteristic lengths $\bar{\ell}$ and σ_g given by equations (20, 21), respectively. Figure 2 shows the density profile (36) for $L = 15\sigma$ and different values of σ_g and N. For $\sigma_g > \bar{\ell}$ both parameters influence the profile. In this case, the onset of a oscillatory structure is governed by $\bar{\ell}$ (absence of structure for large values of $\bar{\ell}$ and increasing number of oscillations as $\bar{\ell}$ tends to zero), while the symmetry of the profile is governed by σ_g (for $\sigma_g \gg \bar{\ell}$ the profile is practically symmetrical about the centre of

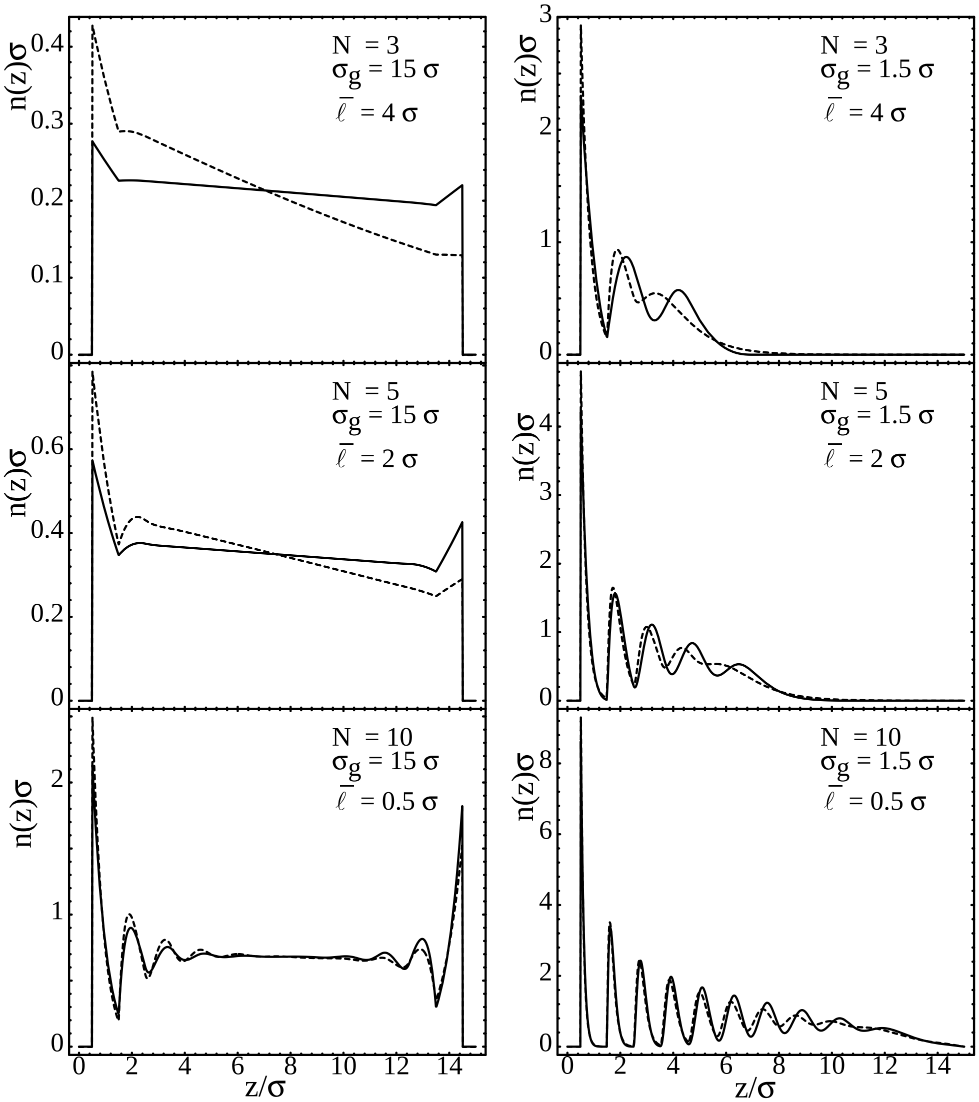

Fig. 2. Microcanonical (solid lines) and canonical (dashed lines) number density $n(z)$ as a function of height z, for $N = 3, 5$ and 10. Microcanonical curves have been obtained from (36), while canonical curves have been obtained from expression (A1) of reference [3] for the corresponding values of k_BT/mg given by (23). For the cases of the left column $\sigma_g = L$ while for the cases of the right column $\sigma_g = 0.1L$. In all cases $L = 15\sigma$, $z_0 = -\sigma/2$ and the distances are measured in units of rod length (σ).

the box showing slight deviations from the profile density (39) in absence of gravity; the asymmetry increases as σ_g decreases). For $\sigma_g < \bar{\ell}$, the hard rods have not enough energy to reach the top wall, so that the profile density becomes $\bar{\ell}$-independent and its shape is only governed by σ_g. In this case, as σ_g decreases the number of oscillations increases, compressing the oscillatory structure to the bottom wall direction and showing an exponential decay to zero with height. Figure 2 also shows the canonical density profiles obtained from the expression reported by Ibsen *et al.* [3] for the corresponding values of k_BT/mg obtained from (23). One can see that microcanonical density profiles approach the canonical ones as σ_g and N increase.

The contact values of the microcanonical number density follow from (36) by taking into account that for $z = z_0 + \sigma$ and for $z = z_{N+1} - \sigma$ only the terms $j = 1$ and $j = N$, respectively, contribute to the sum over j. One easily finds:

$$n(z_0 + \sigma) = mg\left(\frac{3N}{2} - 1\right)\left[\frac{N\phi_N(E - mg\alpha, mg\bar{L}, 0, 2)}{\phi_N(E - mg\alpha, mg\bar{L}, 0, 1)} - \frac{\phi_N(E - mg\alpha, mg\bar{L}, 1, 2)}{\phi_N(E - mg\alpha, mg\bar{L}, 0, 1)}\right], \quad (40)$$

$$n(z_{N+1} - \sigma) = - mg\left(\frac{3N}{2} - 1\right)\frac{\phi_N(E - mg\alpha, mg\bar{L}, 1, 2)}{\phi_N(E - mg\alpha, mg\bar{L}, 0, 1)}, \quad (41)$$

where we have used (13), and $\phi_N(a, b, n, \nu)$ is given by (12). By comparing expressions equations (40, 41) with

$$n^{(k)}(z_1,...,z_k)=\frac{(2\pi m)^{N/2}}{h^N(mg)^{N-k}\Gamma\left(\frac{3N}{2}-k+1\right)\Omega(z_0,z_{N+1};N)}\sum_{i_1<...<i_k}\frac{1}{\Gamma(i_1)\Gamma(i_2-i_1)...\Gamma(N-i_k+1)}$$
$$\times\sum_{j_1=0}^{i_1-1}\sum_{j_2=0}^{i_2-i_1-1}...\sum_{j_{k+1}=0}^{N-i_k}(-1)^{j_1+...+j_{k+1}}\binom{i_1-1}{j_1}\binom{i_2-i_1-1}{j_2}...\binom{N-i_k}{j_{k+1}}$$
$$\times\left[E-mg\sum_{i=1}^{k}z_i-mgb_{i_1,..,i_k}-j_1mg\xi_{i_1}-\sum_{n=2}^{k}j_img(\xi_{i_n}-\xi_{i_{n-1}})-j_{k+1}mg(\bar{L}-\xi_{i_k})\right]^{\frac{3N}{2}-k-1}$$
$$\times\Theta\left[E-mg\sum_{i=1}^{k}z_i-mgb_{i_1,..,i_k}-j_1mg\xi_{i_1}-\sum_{i=2}^{k}j_img(\xi_{i_n}-\xi_{i_{n-1}})-j_{k+1}mg(\bar{L}-\xi_{i_k})\right]$$
$$\times\Theta(\xi_{i_1})\Theta(\xi_{i_2}-\xi_{i_1})...\Theta(\bar{L}-\xi_{i_k})\,. \quad (49)$$

equations (26, 27), respectively, one finds that the contact values of the number density are not proportional to the forces on the corresponding wall when these forces are derived from the entropy definition (15). This was expected, since the number density $n(z)$ has been derived from a microcanonical average while the entropy definition (15) is based on the theorem of adiabatic invariance of the phase volume and not on a microcanonical average. An entropy definition based in an ensemble average is the Gibbs entropy

$$S=-k_B\langle\ln\rho\rangle=k_B\,\ln\Omega\,, \quad (42)$$

where $\rho=\Omega^{-1}\delta\,(E-\mathcal{H})$ is the microcanonical density function. From (42), and using (13), we obtain:

$$\left(\frac{1}{k_BT}\right)_\Omega=\left(\frac{\partial\ln\Omega}{\partial E}\right)_{L,N}=\left(\frac{3N}{2}-1\right)\frac{\phi_N(E-mg\alpha,mg\bar{L},0,2)}{\phi_N(E-mg\alpha,mg\bar{L},0,1)}\,, \quad (43)$$

$$\left(\frac{F_b}{k_BT}\right)_\Omega=-\frac{\partial\ln\Omega}{\partial z_0}=mg\left(\frac{3N}{2}-1\right)\left[\frac{N\phi_N(E-mg\alpha,mg\bar{L},0,2)}{\phi_N(E-mg\alpha,mg\bar{L},0,1)}-\frac{\phi_N(E-mg\alpha,mg\bar{L},1,2)}{\phi_N(E-mg\alpha,mg\bar{L},0,1)}\right]\,, \quad (44)$$

$$\left(\frac{F_t}{k_BT}\right)_\Omega=\frac{\partial\ln\Omega}{\partial z_{N+1}}=-mg\left(\frac{3N}{2}-1\right)\frac{\phi_N(E-mg\alpha,mg\bar{L},1,2)}{\phi_N(E-mg\alpha,mg\bar{L},0,1)}, \quad (45)$$

where the subscript Ω denotes the use of the entropy definition (42). Notice that equations (44, 45) coincide now with the contact values equations (40, 41), respectively. From equations (43–45) we also obtain

$$(F_b)_\Omega=mgN\left[1-\frac{\phi_N(1,y,1,2)}{N\phi_N(1,y,0,2)}\right]\,, \quad (46)$$

$$(F_t)_\Omega=-mg\frac{\phi_N(1,y,1,2)}{N\phi_N(1,y,0,2)}\,, \quad (47)$$

so that $(F_b-F_t)_\Omega=mgN$. As it is well-known definitions (15, 42) for the entropy agree to order $\ln(N)$, and so one can check that expressions (23, 43) for the temperature, equations (26, 44) for the force on the bottom wall, and equations (27, 45) for the force on the top wall, are in agreement to order $1/N$ and so they are equivalent in the thermodynamic limit.

Higher order molecular distribution functions can be derived in a similar way from their definition as a microcanonical ensemble average

$$n^{(k)}(z_1,...,z_k)=\left\langle\sum_{i_1,...,i_k}\delta(z_{i_1}-z_1)...\delta(z_{i_k}-z_k)\right\rangle\,, \quad (48)$$

where, since the coordinates verify the relation $z_1<...<z_k$, only the terms satisfying $i_1<...<i_k$ contribute to the sum. Following the same procedure as in the derivation of (36), we obtain:

see equation (49) above

where

$$b_{i_1,..,i_k}=(i_1-1)z_0+(i_2-i_1)z_1+...+(N-i_k)z_k+\frac{(i_1-1)i_1}{2}\sigma+\frac{(i_2-i_1)(i_2-i_1+1)}{2}\sigma+...+\frac{(N-i_k)(N-i_k+1)}{2}\sigma\,, \quad (50)$$

$$\xi_{i_n}=z_n-z_0-i_n\sigma\,. \quad (51)$$

One easily checks that (49) reduces to (36) for $k=1$.

5 Conclusions

Since statistical ensembles are equivalent in the thermodynamic limit, the thermodynamic study of any exactly solvable system model can be made in any of them. The election of an specific ensemble is usually related with the complications arising from analytic work. In this way, although one might consider the microcanonical ensemble as the more fundamental description of a system (since it does not require the consideration of any kind of reservoir), the canonical and grand canonical ensembles are more usual than the microcanonical one. However, when different ensembles are applied to systems with a small number of particles the obtained results can be different, and there is an intrinsic interest in analyzing the difference between those results (the so-called *explicit* size effects). This analysis can be of importance not only for the correct interpretation of computer simulation results but also for systems confined to regions of molecular size.

In the above context, this paper has been devoted to apply the microcanonical ensemble framework to the study of a system of hard rods confined in a linear box of finite length in the presence of a uniform gravitational field. A thermodynamic analysis of this system, including molecular distribution functions, has been recently reported by Ibsen *et al.* [3] both in the canonical and in the grand canonical ensembles. Therefore, this paper is somewhat complementary to the work of these authors.

The main results of the present paper are the following: (1) Derivation of explicit expressions for the phase volume and the density of states. Calculations are based on the use of the Laplace transform technique to perform the phase integrals over the configurational coordinates. (2) Closed expressions for the entropy, the temperature, the forces exerted on the fluid by the end walls, and the heat capacity are derived. A key parameter in the behaviour of these quantities is $y = \bar{\ell}/\sigma_g$, where $\bar{\ell}$ and σ_g are characteristic lengths associated to the space and the energy available per hard rod, respectively. Entropy, temperature and heat capacity show the same behaviour with y than the ones previously reported for the ideal gas case [5], while the microcanonical force on the bottom (top) wall increases (decreases) as y decreases approaching quickly to the canonical result as N increases. (3) Closed expressions for the number density $n(z)$ at a given height z and for higher order molecular distributions are derived from their definitions as microcanonical ensemble averages. A detailed study of the dependence of $n(z)$ on the two characteristic lengths $\bar{\ell}$ and σ_g is presented. For values of σ_g smaller than $\bar{\ell}$ the profile is $\bar{\ell}$-independent with increasing oscillatory structure as σ_g decreases, while for values of σ_g greater than $\bar{\ell}$ both parameters influence the profile. A comparison with the canonical number density shows that microcanonical and canonical profiles approach as σ_g and N increase. (4) The number density at the ends of the box (contact values) are proportional to the forces exerted by the fluid on the corresponding wall when these forces are derived from the entropy definition in terms of the density of states, but not to the forces derived from the entropy definition in terms of the phase volume. This shows an interesting example about the ambiguity of the entropy definition in the microcanonical ensemble.

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