Hard rods in the presence of a uniform external field

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We sum the canonical partition function for a system of hard rods in a box of finite length in the presence of a linear external potential (gravity). From the canonical partition function closed expressions for the pressure at the top and bottom walls, and the chemical potential follow. The canonical number density and higher distribution functions are also determined. In particular it is shown that the number densities at the extremes of the box are proportional to the associated pressures at those points even though this is not generally true in the bulk of the system. It also is shown that the system is naturally divided in two *wall zones* and, if the density is low enough, a *central zone* as it is the case for the free field system. An expression for the local pressure is also derived and it is found that, in the thermodynamic limit and in a sufficiently weak external potential, an exact local relation between the number density and the pressure profile (equation of state) exists in the canonical ensemble within the central region. We also compute the grand canonical partition function for the system and generalize some results from other authors. © *1997 American Institute of Physics.* [S0021-9606(97)50236-4]

I. INTRODUCTION

One dimensional systems have often been a source for exact results.[1,2] In the case of uniform or inhomogeneous fluids the hard rod system has proved to be useful and has been revised from time to time.[2,3] Its equation of state was first derived by Rayleigh,[4] and rediscovered some time later by Tonks.[5] The distribution functions for the homogeneous system in the thermodynamic limit were first calculated by Salsburg *et al.*,[6] and later Leff *et al.* obtained the number and pair densities for a system confined to a finite length using in the canonical ensemble.[7] Robledo *et al.*[8] studied the finite length effects on the equilibrium properties of the hard rod fluid and they found a relation between the distribution functions and the grand canonical partition function. Davis[9] generalized this last result to a system under the presence of an arbitrary external field, but explicit calculations were made only for the free field case. An equation for the density profile for hard rods in an arbitrary external field was derived by Percus[10] while Vanderlick *et al.* showed that Percus' equation admits an analytic solution.[11]

The present work deals with a hard rod fluid in the presence of a linear external potential that we call gravity. Both the canonical and grand canonical formalisms are developed. For the canonical ensemble it is found that the system is naturally divided in two or three regions: two walls zones and a *central zone* as it is also the case for the free field system.[7] The latter exist only under certain conditions. The main achievements of the present work are: (i) derivation of a closed form for the canonical partition function. From it generalizations of results already known for the null external field follow. The canonical distribution functions of the system are also derived and in particular the number density function $n(x)$ is carefully studied. (ii) An explicit closed form for the canonical local pressure is derived from the knowledge of $n(x)$ and the pair distribution function. (iii) The existence of a local equation of state is then addressed and it is shown that only if the strength of the external field is sufficiently weak does a local equation of state exist in the thermodynamic limit and only in the central zone. As far as we know this is the first time where the existence of a local equation of state can be explicitly shown for a nonideal gas. (iv) In the grand canonical ensemble a simple relation is found between the grand partition function and the local pressure.

The paper is organized as follows: In section II we sum the canonical partition function and generalize some thermodynamic relations valid for the zero field system. In section III the canonical molecular distribution functions are calculated emphasizing the number density profile features. In section IV we compute the pressure profile and consider the existence of a local equation of state. In section V some relations regarding the grand canonical ensemble will be shown. In section VI we summarize our main results with some additional comments. The explicit formulae for the canonical number density, pair distribution function and pressure profile for the system are displayed in the appendix at the end of the article.

II. CANONICAL ENSEMBLE

Let us consider a fluid composed of hard rods, i.e. interacting through the pair potential

$$u(x)=\begin{cases}\infty, & |x|<\sigma,\\ 0, & |x|\geqslant\sigma,\end{cases}\tag{1}$$

where σ is the length of each rod. The system has N particles (rods) confined to a ''volume'' of length L (Fig. 1) under the presence of a uniform external field of strength g which we call gravity.

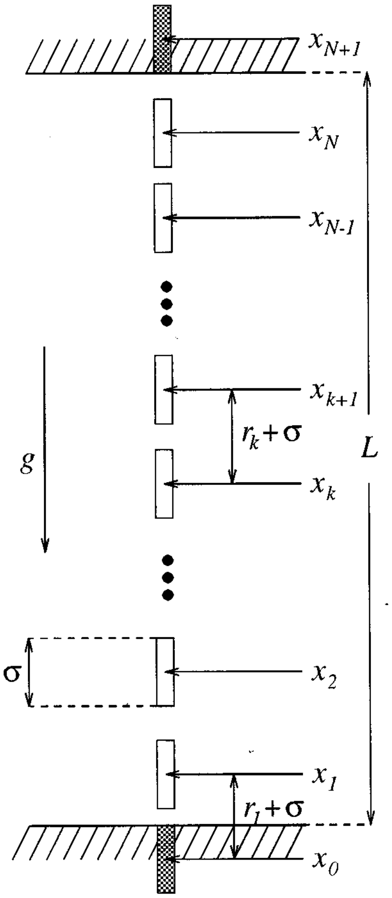

FIG. 1. Hard rod fluid between elastic hard walls. The particles are confined to a ''volume'' of length L, and a uniform external field is present.

Due to the particular form of the interaction, the Boltzmann factor reduces just to a Heaviside step function, defined as the unity for positive values of the argument and zero otherwise,

$$\exp(-\beta u(x))=\theta(x-\sigma), \tag{2}$$

and then the configurational partition function for the system is just

$$Z_N(x_0,x_{N+1})=\int_{x_0}^{x_{N+1}-\sigma}dx_N\cdots\int_{x_0}^{x_{k+1}-\sigma}dx_k\cdots\int_{x_0}^{x_2-\sigma}dx_1\prod_{k=0}^{N}\theta(x_{k+1}-x_k-\sigma)\times\exp\left(-\beta mg\sum_{k=1}^{N}x_k\right) \tag{3}$$

where $x_1\leqslant x_2\cdots\leqslant x_{N-1}\leqslant x_N$ are the positions of the centers of the particles and x_0 and x_{N+1} are the positions of the centers of fixed particles that define the bottom wall and the top walls, respectively. They satisfy $x_{N+1}-x_0=L+\sigma$ as it is illustrated in Fig. 1. The parameter β is the reciprocal of k_BT where k_B is the Boltzmann's constant and T is the absolute temperature. The difference between the position of the last particle and the floor particle satisfy the inequality

$$L\geqslant x_N-x_0. \tag{4}$$

The evaluation of the partition function can be done introducing variables $r_k=x_k-x_{k-1}-\sigma$, $k=1,\ldots,N$. From (4), the relative distances r_k satisfy

$$\ell\geqslant\sum_{k=1}^{N}r_k, \tag{5}$$

where $\ell=L-N\sigma$ correspond to the reduced volume and the integration has to be done over all positive values of r_k compatible with (5). The configurational partition function then becomes

$$Z_N(x_0,x_{N+1})=\exp\left(-\beta mg\left(Nx_0+\sigma\frac{N(N+1)}{2}\right)\right)\times\int_0^\infty dr_1\cdots\int_0^\infty dr_N\theta\left(\ell-\sum_{k=1}^{N}r_k\right)\times\prod_{k=1}^{N-1}\theta(r_k)\exp\left(-\beta mg\sum_{k=1}^{N}(N-k+1)r_k\right). \tag{6}$$

All the Heaviside functions evaluated in the variables r_k are equal to unity since r_k goes from 0 to infinity in each integral. Replacing the remaining Heaviside function by its integral representation,

$$\theta(x)=\frac{1}{2\pi i}\int_{-i\infty+\tau_0}^{i\infty+\tau_0}\frac{dp}{p}\exp(px), \tag{7}$$

and reverting the order of integration each one can be easily evaluated. The final result is

$$Z_N(x_0,x_{N+1})=\exp\left(-\beta mg\left(Nx_0+\sigma\frac{N(N+1)}{2}\right)\right)\times\frac{1}{N!}\left(\frac{1-\exp(-\beta mg\ell)}{\beta mg}\right)^N\theta(\ell). \tag{8}$$

The configurational partition function Z_N depends on x_{N+1} through the relation $\ell=x_{N+1}-x_0-(N+1)\sigma$.

As the strength of the gravitational field vanishes the usual partition function for hard rods is recovered.[1] On the other hand, for any finite value of βmg the partition function explicitly depends on the position of the bottom molecule and, if the length of the box goes to infinity, the only relevant length scale for the system is

$$\sigma_g=\frac{k_BT}{mg}. \tag{9}$$

The thermodynamics of the system can now be easily computed from the canonical partition function. The Helmholtz free energy for the system is

$$A=k_BTN\log\Lambda+mgNx_0+mg\sigma\frac{N(N+1)}{2}$$
$$-k_BTN\log\left(\frac{1-\exp(-\beta mg\ell)}{\beta mg}\right), \tag{10}$$

where Λ is the De Broglie wavelength. The pressure (force) on each one of the walls can be computed simply by taking the partial derivative with respect to the position of these walls. The force exerted on the fluid by the bottom wall is

$$F_b=\frac{\partial A}{\partial x_0}=mgN\left(1+\frac{\exp(-\beta mg\ell)}{1-\exp(-\beta mg\ell)}\right), \tag{11}$$

and the forced exerted on the top wall by the fluid is

$$F_t=-\frac{\partial A}{\partial x_{N+1}}=mgN\frac{\exp(-\beta mg\ell)}{1-\exp(-\beta mg\ell)}. \tag{12}$$

Their difference is the weight of the system as expected. Due to the presence of gravity the pressure field is no longer uniform. Equation (11) can be simply interpreted as the hydrostatic pressure plus an additional term that is related to the existence of the upper wall. If the position of the upper wall goes to infinity, the fluid exerts no force on it and the pressure on the bottom wall is just the hydrostatic term. Taking the limit $g\to 0$ yields the well known equation of state[1,4,5]

$$F_b=F_t=k_BT\frac{N}{L-N\sigma}. \tag{13}$$

Taking the derivative of equation (10) with respect to N the dependence of the chemical potential μ on g is found to be

$$\beta\mu=\beta mgx_0+\beta mg\sigma(N+1/2)$$
$$+\beta mgN\sigma\frac{\exp(-\beta mg\ell)}{1-\exp(-\beta mg\ell)}$$
$$+\log\left(\frac{\beta mgN\Lambda}{1-\exp(-\beta mg\ell)}\right). \tag{14}$$

Introducing the reduced fugacity as $\zeta=\exp(\beta\mu)/\Lambda$ and using equations (11) and (12) the following relation is found

$$\zeta=\exp(\beta mgx_0)\exp(\beta mg(N+1/2)\sigma)\frac{F_b}{k_BT}\exp\left(\frac{F_t\sigma}{k_BT}\right). \tag{15}$$

As the parameter βmg goes to zero the pressure becomes uniform and the relation found by Robledo *et al.*[8] is reobtained.

III. CANONICAL MOLECULAR DISTRIBUTION FUNCTIONS

The number density at a given height x can be computed from both its definition as an ensemble average,

$$n(x)=\left\langle\sum_{k=1}^{N}\delta(x_k-x)\right\rangle, \tag{16}$$

or from the evaluation of the well known functional derivative

$$n(x)=\left.\frac{\delta A}{\delta v(x)}\right|_{v(x)=mgx}. \tag{17}$$

In the expression above $v(x)$ is an arbitrary external field which has to be evaluated to $v(x)=mgx$ after differentiation. This functional derivative yields the well known factorization[12]

$$n(x)=\frac{\exp(-\beta mgx)}{Z_N(x_0,x_{N+1})}\sum_{k=1}^{N}Z_{k-1}(x_0,x)Z_{N-k}(x,x_{N+1}). \tag{18}$$

The explicit form for the number density for the hard rod system is displayed in the appendix. The density profile has a structure similar to the case of zero gravity, two border zones of width $(N-1)\sigma$ going from the bottom of the box to $x_0+N\sigma$ and from $x_{N+1}-N\sigma$ to the top of the box, plus a central zone that exists only if $N\leqslant(L+\sigma)/2\sigma$. The behavior of the density profile is dominated by the characteristic length σ_g introduced in equation (9). For values of σ_g greater than the length of the box the number density is just slightly modified from the zero gravity case. As σ_g decreases (larger g) the particles move to the bottom of the vessel, increasing the number of density oscillations and compressing the oscillatory structure in the same direction. For σ_g small enough, with respect to the length of the box, the particles never reach the upper wall and the behavior of the system is just the same as a fluid confined to smaller region. The density decreases exponentially down to zero with height in this case. The dependence on the position of the bottom wall is trivial because it is just a shift in the choice of the origin of coordinates. Figure 2 shows the number density for 10 rods and some values of σ_g and L.

The contact values of the density are

$$\lim_{x\to(x_0+\sigma)}n(x)=\frac{\beta mgN}{1-\exp(-\beta mg\ell)}=\frac{F_b}{k_BT}, \tag{19}$$

$$\lim_{x\to(x_{N+1}-\sigma)}n(x)=\beta mgN\frac{\exp(-\beta mg\ell)}{1-\exp(-\beta mg\ell)}=\frac{F_t}{k_BT}, \tag{20}$$

which means that these values of the number density are proportional to the pressure exerted by the fluid to the wall. This generalizes a relation found by Robledo *et al.*[8]

Higher order distribution functions can be determined in a similar fashion from their definition in the canonical ensemble

$$n^{(k)}(x_1,\ldots,x_k)=\left\langle\sum_{j_1,\ldots,j_k}\delta(x_{j_1}-x_1)\cdots\delta(x_{j_k}-x_k)\right\rangle. \tag{21}$$

Due to the hard rod repulsive nature of the potential the particle order remains unchanged during the evolution. Hence if the coordinates satisfy the relation $x_1<\cdots<x_k$, only the terms satisfying $j_1<\cdots<j_k$ contribute to the sum,

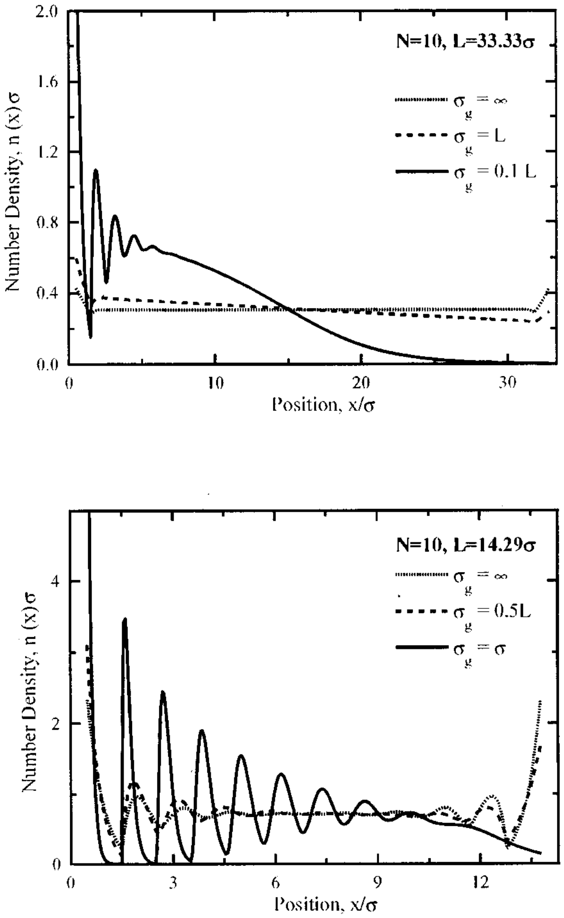

FIG. 2. Number density as a function of height x. The top figure shows a system with reduced bulk density $N\sigma/L = 0.3$ while the bottom figure shows a system with $N\sigma/L = 0.7$. In both cases the origin is at the bottom wall ($x_0 = -\sigma/2$) and the distances are measure in units of rod length.

$$n^{(k)}(x_1,\ldots,x_k) = \left\langle \sum_{j_1<\cdots<j_k} \delta(x_{j_1}-x_1)\cdots\delta(x_{j_k}-x_k) \right\rangle. \tag{22}$$

The function $n^{(k)}$ can be computed for all the values of $x_1,\ldots,x_k$ using its symmetry

$$\begin{aligned} &n^{(k)}(x_1,\ldots,x_j,\ldots,x_{j'},\ldots,x_k) \\ &\quad = n^{(k)}(x_1,\ldots,x_{j'},\ldots,x_j,\ldots,x_k), \end{aligned} \tag{23}$$

for all $j,j' = 1,\ldots,k$. Using functional differentiation of the canonical partition function it can be shown that (22) takes the form

$$\begin{aligned} n^{(k)}(x_1,\ldots,x_k) = {} & \exp\left(-\beta \sum_{j=1}^{k} mgx_j \right) \frac{1}{Z_N(x_0,x_{N+1})} \\ & \times \sum_{j_1<\cdots<j_k} Z_{j_1-1}(x_0,x_1) \\ & \times Z_{j_2-j_1-1}(x_1,x_2)\cdots Z_{j_k-j_{k-1}-1} \\ & \times (x_{k-1},x_k) Z_{N-j_k}(x_k,x_N), \end{aligned} \tag{24}$$

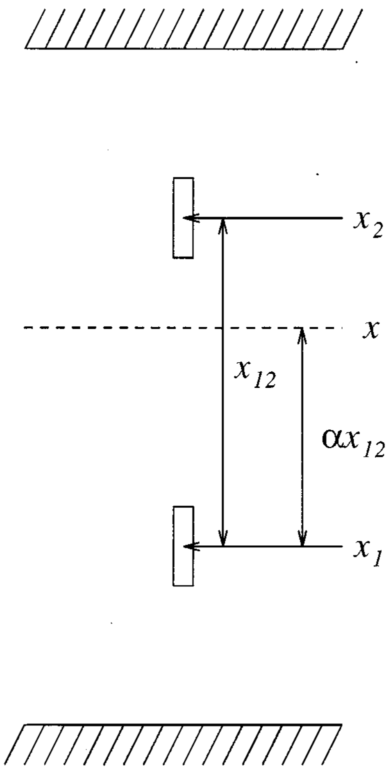

FIG. 3. The non-ideal contribution to the local pressure can be computed making a detailed balance of the intermolecular forces that cross the imaginary point located at x.

and then all the canonical molecular distribution functions can be computed from the configurational partition function. An explicit expression for the pair distribution function is displayed in the appendix.

IV. LOCAL PRESSURE AND A LOCAL EQUATION OF STATE

The local pressure can be evaluated from the knowledge of the density and the pair distribution function. The kinetic contribution to the pressure is the same as in the ideal case, i.e., $k_B T$ times the number density. The intermolecular contribution can be computed in the one dimensional case following the mechanical arguments due to Irving *et al.* and others,[13] and they are reproduced here for completeness. Following their arguments, let us divide the space in two regions, below (zone 1) and above (zone 2) some height x, as shown in Fig. 3.

The force that a molecule at x_2 in zone 2 senses, due to the presence of a molecule at x_1 in zone 1, is

$$F_{21} = -\operatorname{sgn}(x_{12}) u'(|x_{12}|), \tag{25}$$

where $x_{12} = x_2 - x_1$. The mean number of particle pairs positioned at x_1 and x_2 is proportional to the pair distribution function evaluated at those positions. We can refer those positions to the height x as $x_1 = x - \alpha x_{12}$ and $x_2 = x + (1-\alpha)x_{12}$ where α is the ratio between $x - x_1$ and x_{12} and satisfies $0 \leqslant \alpha \leqslant 1$. For a fixed value of x_{12} the volume element where particle 1 has to be located in order that the length αx_{12} ends in x is $x_{12} d\alpha$. The mean number of pairs with particle 1 between x_1 and $x_1+|x_{12}|d\alpha$ and particle 2 between x_2 and x_2+dx_{12} is

$$n^{(2)}(x-\alpha x_{12},x+(1-\alpha)x_{12})|x_{12}|d\alpha dx_{12}. \tag{26}$$

The force felt at a given height x due to the intermolecular interaction between the molecules is

$$F_c(x)=-\int_0^\infty dx_{12}\int_0^1 d\alpha \operatorname{sgn}(x_{12})u'(|x_{12}|)n^{(2)}(x-\alpha|x_{12}|,x+(1-\alpha)|x_{12}|)|x_{12}|, \tag{27}$$

and then the pressure of the fluid at height x is given by

$$F(x)=k_BTn(x)-\int_0^\infty dx_{12}\int_0^1 d\alpha u'(x_{12})n^{(2)}(x-\alpha x_{12},x+(1-\alpha)x_{12})x_{12}. \tag{28}$$

It was shown by Schofield *et al.*[14] that the pressure is not uniquely determined, and that its form depends on the path chosen to join the interacting molecules. Only in the one dimensional case the local pressure is unique as there is no room for such ambiguity. For hard rods this equation is reduced to

$$F(x)=k_BTn(x)+k_BT\sigma\int_0^1 d\alpha n^{(2)}(x-\alpha\sigma,x+(1-\alpha)\sigma), \tag{29}$$

and it is straightforward to see that the collisional contribution vanishes at the ends of the box because the pair distribution function is zero for values of its arguments outside the system. This is consistent with relations (11) and (12) between the pressure and the contact number density.

The elastic hard collision between the rods yields a simple exchange of their velocities or, in an equivalent picture, one could equally well relabel the particles in each collision and think that they pass through each other without altering their speed. From this second viewpoint apparently then the system is equivalent to one of noninteracting particles and therefore the pressure should be of pure kinetic origin contrary to what (29) states. This is not so and the gas is not totally trivial because either the particles bounce back, exchanging their velocities, or else they suffer an infinite acceleration that instantaneously displaces them to a new position σ away. In either picture collisions are a nontrivial processes, responsible for the additional term to the pressure.

Evaluating the pair distribution function—see the appendix, equation (A2)—at $x_1=x-\alpha\sigma$ and $x_2=x+(1-\alpha)\sigma$ it is seen that only the nearest neighbor particles contribute to the collisional pressure as expected. The explicit form for the pressure profile is also given in the appendix. Figures 4 and 5 show the collisional and total pressure for 10 molecules and several values of σ_g and L.

The structure of the pressure profile is similar to the number density profile. As it has already been mentioned, three different zones can be distinguished, border zones of width $(N-1)\sigma$ on both extremes of the box and, if the bulk density is low enough, a central zone.

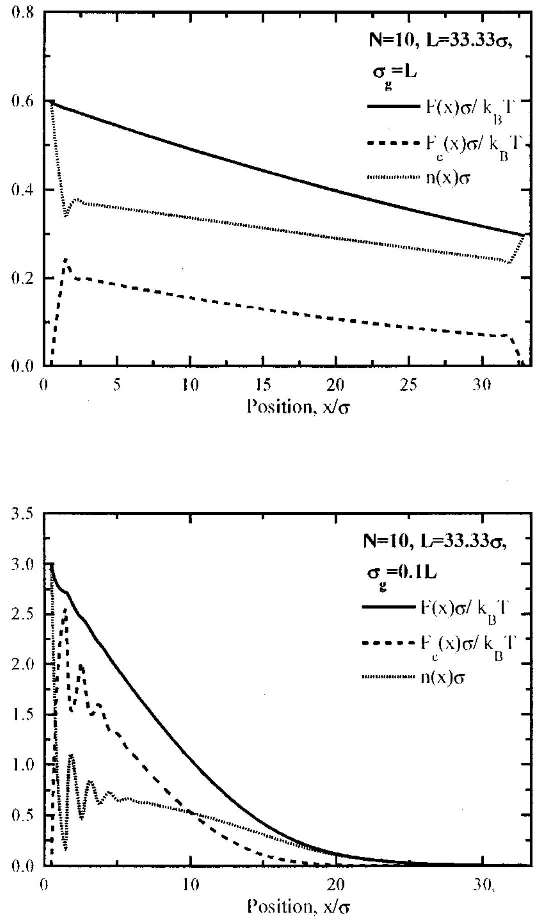

FIG. 4. Pressure profile, collisional pressure and number density versus height x. The number of particles N is 10, the length of the system is 33.33σ and $\sigma_g=L$ (top figure) and $\sigma_g=0.1L$ (bottom figure).

A local equation of state between both profiles arises in two cases: (i) when the density is low enough and (ii) when the length associated to the gravity field, σ_g, is greater than the size of the vessel. In the first case the collisional contribution to the pressure is negligible with respect to the kinetic term and therefore the pressure profile equals $k_BTn(x)$. The second case is the usual local thermodynamic assumption, widely used, for instance, in fluid dynamics,[15] and can be explicitly demonstrated for this system. Indeed, expanding equations (A1) and (A3) to first order in L/σ_g for heights belonging to the central zone and taking the thermodynamic limit, $N,L\rightarrow\infty$ with $n_B=N/L$ constant, the profiles become

$$n(x)=n_B+\frac{L}{\sigma_g}n_B(1-n_B\sigma)^2\left(\frac{1}{2}-\frac{x}{L}\right), \tag{30}$$

$$\frac{F(x)}{k_BT}=\frac{n_B}{1-n_B\sigma}+\frac{L}{\sigma_g}n_B\left(\frac{1}{2}-\frac{x}{L}\right), \tag{31}$$

and then the pressure and density profiles are related through

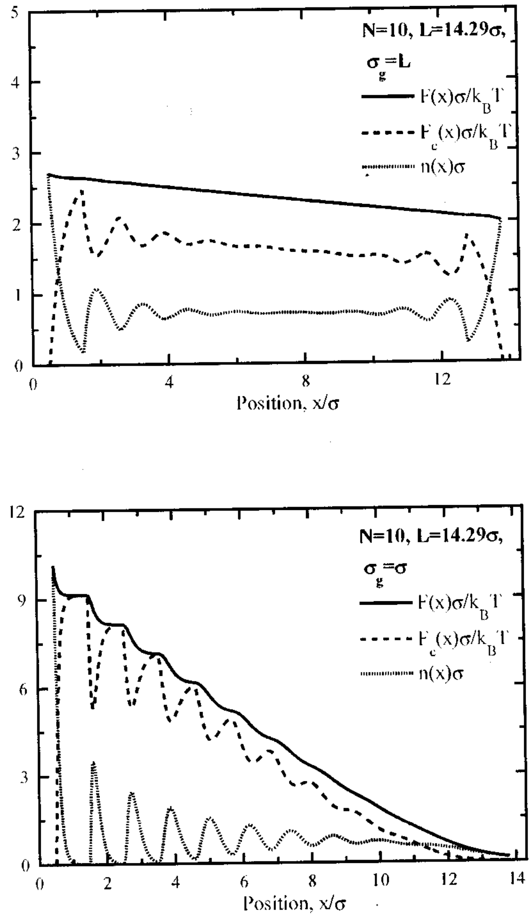

FIG. 5. Pressure profile, collisional pressure and number density versus height x. The length of the system is 14.29σ and $\sigma_g = L$ (top figure) and $\sigma_g = \sigma$ (bottom figure). The reduced bulk density $N\sigma/L = 0.7$ in this case and therefore there is no central zone.

$$\frac{F(x)}{k_B T} = \frac{n_B}{1 - n_B\sigma} + \frac{n(x) - n_B}{(1 - n_B\sigma)^2}, \tag{32}$$

which is the expansion, to first order in $\delta n(x) = n(x) - n_B$ about n_B, of the equation of state for the system with zero gravity. As far as we know this is the first nontrivial system where a local equation of state can be explicitly derived from statistical mechanics arguments. The finite size corrections to equation (32) can be derived straightforwardly from the exact expressions (A5) and (A6) given in the appendix.

V. GRAND CANONICAL ENSEMBLE.

The thermodynamic state of the system in the grand canonical ensemble is defined by the positions of each wall, x_0 and x_{N+1}, the temperature T and the chemical potential μ. The grand canonical potential is

$$\Omega(x_0, x_{N+1}) = -k_B T \log \Xi(x_0, x_{N+1}), \tag{33}$$

where

$$\Xi(x_0, x_{N+1}) = \sum_{N \geqslant 0} \zeta^N Z(x_0, x_{N+1}), \tag{34}$$

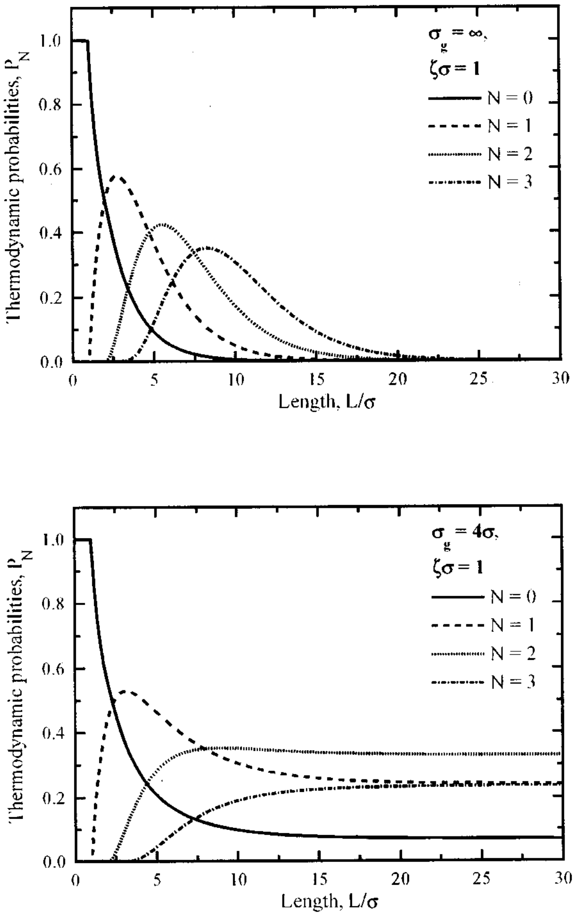

FIG. 6. Probabilities that the system has zero to four particles as a function of L are shown. In both cases the reduced fugacity is unity and $x_0 = -\sigma/2$. In the top figure the probabilities go to zero with L. In the lower figure the probabilities reach a stationary value because of the finite value of σ_g.

where ζ is the reduced fugacity introduced in (15). The thermodynamic probability for a system to have exactly N particles is

$$P_N(x_0, x_{N+1}) = \frac{\zeta^N Z(x_0, x_{N+1})}{\Xi(x_0, x_{N+1})}. \tag{35}$$

In the absence of gravity the probabilities P_N are functions of L and ζ only. However, for nonvanishing g these probabilities are also functions of x_0 and σ_g, i.e., different systems can be distinguished by the position of the bottom wall. For zero gravity and a fixed value of ζ, all probabilities go to zero as L increases. If instead the value of σ_g is finite, they all reach a stationary value as L grows (see Fig. 6), as can be readily seen using equations (8) and (35).

As a consequence for a fixed value of g the mean number of particles reaches an asymptotic value when the size of the system is just a few times the associated length σ_g (see Fig. 7, top). This result can be derived intuitively recalling that the velocity distribution function for the system does not depends on L. Since we have fixed the temperature, the larger velocities needed to reach the top wall as L grows will be very unlikely, and hence almost all the particles will be

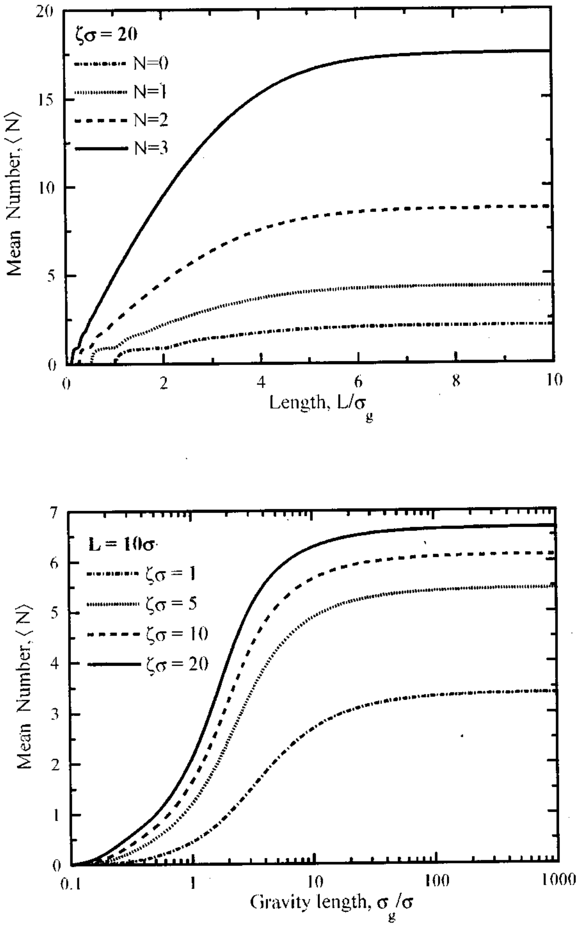

FIG. 7. Top: For finite values of σ_g the mean number of particles saturates as L increases. The reduced fugacity in all cases has been set to $20/\sigma$ and $x_0=-\sigma/2$. Bottom: The mean number of particles goes to zero as gravity increases (vanishing σ_g), and then most of the molecules will be at the particles bath surrounding the system.

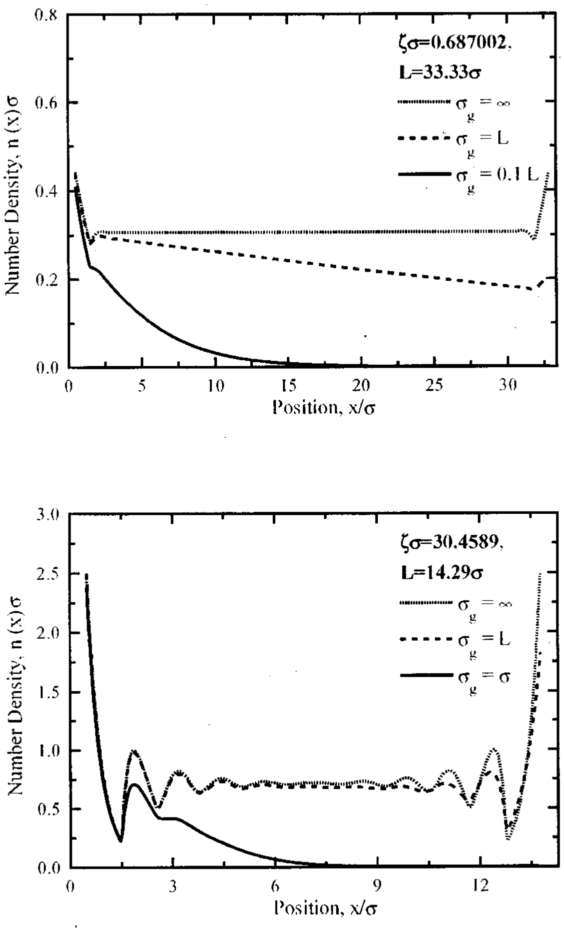

FIG. 8. Density profiles in the grand canonical ensemble. In both cases the fugacity has been set to give 10 particles for the zero gravity system. If ζ is kept fixed, the mean number of particles decreases as σ_g increases.

below that wall. The asymptotic mean number depends on, besides σ_g, the position of the bottom wall and the reduced fugacity. It does not scale linearly with L as is the case for vanishing gravity. On the other hand, keeping x_0, L and ζ fixed, the average $\langle N\rangle$ is a strictly increasing function of σ_g (see Fig. 7, bottom). This is intuitive because as gravity increases less particles pass from the particle bath to the system.

The mean number of particles for a box of length $L+\sigma$ can be related to averages of quantities for a box of length L and therefore an expression for the reduced fugacity can be found. It is

$$\zeta=\exp(\beta mgx_0)\langle\exp(-\beta mg(N+1/2)\sigma)\rangle_{x_0,L}^{-1}$$
$$\times\frac{\beta mg\langle N\rangle_{x_0,L+\sigma}}{\langle 1-\exp(-\beta mg\ell)\rangle_{x_0,L}}$$
$$\times\exp(\beta mg\sigma/2)\,\frac{\Xi(x_0,x_{N+1}+\sigma)}{\Xi(x_0,x_{N+1})}. \tag{36}$$

It generalizes the result found by Robledo *et al.*[8] and it has a resemblance to equation (15) found in the canonical ensemble.

The number density and higher distribution functions in the grand canonical ensemble can be obtained from the expressions derived by Davis,[9] adapted to the presence of a gravitational field. They are

$$n^{(k)}(x_1,\ldots,x_k)=\exp\left(-\beta mg\sum_{j=1}^{k}x_j\right)\frac{\zeta^k}{\Xi(x_0,x_N+1)}$$
$$\times\Xi(x_0,x_1)\prod_{j=2}^{k}\Xi(x_{j-1},x_j)\Xi(x_k,x_{N+1}). \tag{37}$$

Figure 8 shows the number density profiles for some values of ζ and σ_g. As σ_g goes to zero with fixed ζ, the density profile shows less density oscillations than the canonical counterpart. The reason for this is that there is an exchange of particles between the system and a reservoir. Hence the mean number of molecules decreases as σ_g increases.

The pressure profile has a simple expression in terms of the grand canonical partition function also,

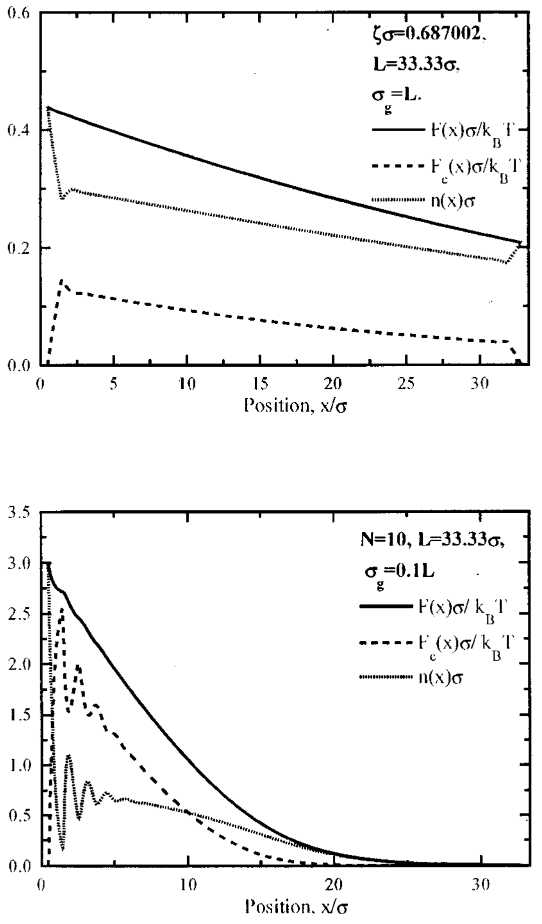

FIG. 9. The pressure profile, collisional contribution and number density are shown. The reduced fugacity was set to give 10 particles in the free field case. In the top figure the bulk density $\langle N\rangle\sigma/L=0.231$ and the collisional contribution to the pressure is always present. In the bottom figure the gravity field is strong and then for heights beyond a determined value the nonideal contribution to the pressure is negligible. The bulk density $\langle N\rangle\sigma/L=0.041$ in this case.

$$\frac{F(x)}{k_BT}=n(x)+\zeta^2\sigma\exp(-2\beta mgx)\int_0^1 d\alpha\exp(-\beta mg(1-2\alpha)\sigma)\frac{\Xi(x_0,x-\alpha\sigma)\Xi(x+(1-\alpha)\sigma,x_{N+1})}{\Xi(x_0,x_{N+1})}. \tag{38}$$

It shows that the collisional pressure decays to zero faster with height than the number density. Figure 9 shows the pressure profile and the nonideal contribution to the pressure for two values of ζ and some values of σ_g.

In the grand canonical ensemble no central zone exists for finite length because the number density and pressure profiles both have contributions from all the canonical profiles from one molecule to the largest number of particles that the system allows.

VI. CONCLUSIONS

Our main results for the canonical ensemble can be summarized as follows: (i) A closed form for the partition function is found and from it the number density, the pair distribution function and higher distribution functions are derived. (ii) The contact number density density, i.e., the number density at the extremes of the box, is proportional to the forces exerted on each wall by the fluid and this result generalizes the zero field case where the contact number density is proportional to the bulk pressure of the fluid. A similar generalization is achieved for the fugacity of the system, which is now a function of the pressure on each wall and the position of the bottom wall. (iii) The pressure profile can be computed explicitly for the system and, for a sufficiently weak gravity field, a local relation with the density profile in the thermodynamic limit emerges. This relation corresponds to the equation of state for the system with zero gravity. Finite size effects can be directly considered from the exact expressions (A5) and (A6) given in the appendix.

Regarding the grand canonical ensemble, it can be pointed out that the number density shows that if the value of the reduced fugacity is kept fixed and the gravity field increases, the number of density oscillations is smaller that the canonical counterpart. The reason for this is that now the system can exchange particles with an environment and, when gravity becomes stronger, less particles can pass from the particles bath to the system, reducing the mean number of particles. In order to keep the number of particles constant one has to raise the value of the chemical potential.

Finally we would like to remark that besides its academic importance, this result should be useful when comparing approximations in the study of nonuniform fluids. As far as we know this may be the first example of nonuniform fluid, besides the ideal gas, for which all molecular distribution functions can be explicitly computed directly from statistical mechanics arguments.

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APPENDIX: EXPLICIT FORMULAE

(1) Number density:

$$n(x)=\frac{\beta mgN}{(1-\exp(-\beta mg\ell))^N}\sum_{k=1}^{N}\binom{N-1}{k-1}\theta(\xi_k)\times\theta(\ell-\xi_k)\exp(-\beta mg\xi_k)\times(1-\exp(-\beta mg\xi_k))^{k-1}(\exp(-\beta mg\xi_k)\times-\exp(-\beta mg\ell))^{N-k}, \tag{A1}$$

where $\xi_k=\hat{x}-(k-1)\sigma$, and $\hat{x}=x-(x_0+\sigma)$. This equation recovers the result for the number density found by Leff *et al.*[7] when g goes to zero.

(2) Pair distribution function:

$$\begin{aligned} n^{(2)}(x_1,x_2) = {} & \frac{(\beta mg)^2N(N-1)}{(1-\exp(-\beta mg\ell))^N}\sum_{j_2=2}^{N}\sum_{j_1=1}^{j_1-1}\frac{(N-2)!}{(N-j_2)!(j_2-j_1-1)!(j_1-1)!}\theta(\xi_{j_1,1})\theta(\xi_{j_2,2}-\xi_{j_2,2}) \\ & \times\theta(\ell-\xi_{j_2,2})\exp(-\beta mg\xi_{j_1,1})(1-\exp(-\beta mg\xi_{j_1,1}))^{j_1-1}\exp(-\beta mg\xi_{j_2,2})(\exp(-\beta mg\xi_{j_1,1}) \\ & -\exp(-\beta mg\xi_{j_2,2}))^{j_2-j_1-1}(\exp(-\beta mg\xi_{j_1,1})-\exp(-\beta mg\ell))^{N-j_2}, \end{aligned} \tag{A2}$$

where $\xi_{j,k}=x_k-(j-1)\sigma-(x_0+\sigma)$.

(3) Pressure profile:

$$\begin{aligned} F(x) = {} & k_BTn(x)+k_BT\frac{\beta mgN(N-1)}{(1-\exp(-\beta mg\ell))^N}\sum_{k=2}^{N}\binom{N-2}{k-2}\theta(\xi_{k-1})\theta(\ell-\xi_k)\sum_{j=0}^{k-2}\sum_{j'=0}^{N-k}\binom{k-2}{j} \\ & \times\binom{N-k}{j'}\frac{(-1)^{(k-2-j)}}{(N-j-j')}I_{k,j,j'}(\xi_{k-1})(-\exp(-\beta mg\ell))^{j'}, \end{aligned} \tag{A3}$$

where

$$I_{k,j,j'}(x)=\begin{cases} 1-\exp(-\beta mg(N-j-j')x), & x\in[0,\sigma] \\ \exp(-\beta mg(N-j-j')(x-\sigma))-\exp(-\beta mg(N-j-j')x), & x\in[\sigma,\ell] \\ \exp(-\beta mg(N-j-j')(x-\sigma))-\exp(-\beta mg(N-j-j')\ell), & x\in[\ell,\ell+\sigma] \end{cases}, \tag{A4}$$

and ξ_k was introduced in equation (A1).

(4) Number density and pressure profiles expanded to first order in L/σ_g:

$$\begin{aligned} n(x) = {} & \frac{N}{\ell}\sum_{k=0}^{N-1}\frac{(N-1)!}{(N-1-k)!}\frac{(-\sigma)^k}{\ell^k}+\frac{L}{\sigma_g}\left(\frac{N}{L}\sum_{k=0}^{N-1}\frac{(N-1)!}{(N-1-k)!}\frac{(-\sigma)^k}{\ell^k}(k+1)\left[\frac{1}{2}+\frac{(N-1-k)}{2\ell^2}(k+2)\left(\frac{k\sigma^2}{3}-\frac{\sigma^2}{2}\right)-\frac{k\sigma}{2\ell}\right]\right. \\ & \left.+\frac{x}{L}\sum_{k=0}^{N-1}\frac{N!}{(N-1-k)!}\frac{(-\sigma)^k}{\ell^k}(k+1)\left[\frac{(N-(k+1))(k+2)\sigma}{2\ell^2}-\frac{1}{\ell}\right]\right), \end{aligned} \tag{A5}$$

$$\begin{aligned} \frac{F(x)}{k_BT} = {} & \frac{N}{L-N\sigma}+\frac{L}{\sigma_g}\left(\sum_{k=0}^{N-1}\frac{N!}{(N-1-k)!}\frac{(-\sigma)^k}{\ell^{k+1}}\left[-\frac{N(k+1)\sigma}{2}+\frac{(N-1-k)}{2}(k+2)\sigma+\frac{L(k+1)\sigma}{2}\right.\right. \\ & +\frac{(N-1-k)}{2\ell^2}(k+1)(k+2)\left\{(L-(k+2)\sigma)\frac{k\sigma^2}{3}-(L+N\sigma-2(k+2)\sigma)\frac{\sigma^2}{2}\right\}-\frac{(k+1)}{2\ell}k\sigma(L+N\sigma-2(k+1)\sigma) \\ & \left.+\frac{(k+1)}{\ell}\sigma^2(N-1-k)\right]+\frac{x}{L}\sum_{k=0}^{N-1}\frac{N!}{(N-1-k)!}\frac{(-\sigma)^k}{\ell^{k+1}}\left[\frac{(N-1-k)}{2\ell^2}(k+1)(k+2)(L-(k+2)\sigma)\sigma\right. \\ & \left.\left.-\frac{(k+1)}{\ell}(L+N\sigma-2(k+1)\sigma)\right]\right). \end{aligned} \tag{A6}$$

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[1] E. H. Lieb and D. C. Mattis, Editors, *Mathematical Physics in One Dimension* (Academic, New York, 1966).

[2] J. L. Lebowitz, Editor, *Simple Models of Equilibrium and Nonequilibrium Phenomena* (North Holland, Amsterdam, 1987), pp. 5–158.

[3] E. W. Montroll and J. L. Lebowitz, Editors, *The Liquid State of Matter: Fluids, Simple and Complex* (North-Holland, Amsterdam, 1982), pp. 31–140.

[4] Lord Rayleigh, Nature Lond. **45**, 80 (1891).

[5] L. Tonks, Phys. Rev. **50**, 955 (1936).

[6] Z. W. Salsburg, J. G. Kirkwood, and R. W. Zwanzig, J. Chem. Phys. **21**, 1098 (1953).

[7] H. A. Leff and M. J. Coopersmith, J. Math. Phys. **8**, 306 (1967).

[8] A. Robledo and J. S. Rowlinson, Mol. Phys. **58**, 711 (1986).

[9] H. T. Davis, J. Chem. Phys. **93**, 4339 (1990).

[10] J. K. Percus, J. Stat. Phys. **15**, 505 (1976)

[11] T. K. Vanderlick, L. E. Scriven, and H. T. Davis, Phys. Rev. A **34**, 5130 (1986).

[12] J. K. Percus, J. Stat. Phys. **28**, 67 (1982).

[13] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).

[14] P. Schofield and J. R. Henderson, Proc. Roy. Soc. London Ser. A **379**, 231 (1982).

[15] A. L. Fetter and J. D. Walecka, *Theoretical Mechanics of Particles and Continua* (McGraw-Hill, New York, 1980), Chap 9.