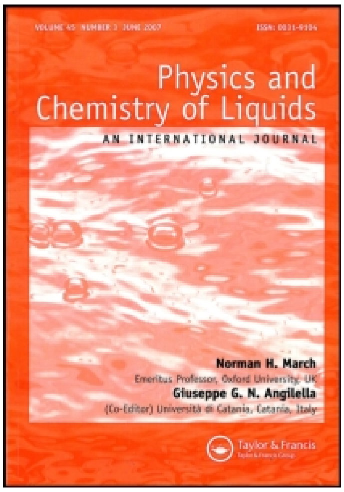

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The Hard Rod Fluid in a Uniform Gravitational Field‡

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Abstract—The system of hard rods in an external, uniform gravitational field is studied and exact expressions obtained for the partition functions, and the one- and two-particle distributions. In principle all higher order distributions can be exactly expressed as finite sums and the Laplace transforms of the one-particle density and pressure for a semi-infinite system are reducible to single integrals. Limiting cases of weak field and small rod diameters are examined. In the former case, these results agree with Percus and Lebowitz's local density expansion. In the latter case, corrections to the barometric pressure and density laws are obtained. Finally some mathematical difficulties involved in the calculation of the virial expansion and distribution of roots of the grand partition function are mentioned.

1. Introduction

Relatively few many body problems can be solved exactly and even these only under the non-physical assumptions of particles moving in one-dimension interacting through nearest neighbor forces. In spite of these limitations we present here an exactly solvable model, classical hard rods in a uniform gravitational field, which may retain some aspect of reality, in that the density–height relationship for a perfect gas is truly one-dimensional, and in the present system the hard rods are aligned in the direction of the field.

We calculate the pressure and density functions for this inhomogeneous system, and show that the local relation which holds for the perfect gas is no longer generally true. In the small hard rod diameter limit one can obtain corrections to these "barometric laws".

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2. Calculation of Partition Function

Consider N particles on a line L interacting through nearest neighbor forces

$$\phi = \sum_{i,j=0}^{N+1}{}' \phi(x_i - x_j)$$

and in an external potential

$$U = \sum_{i=1}^{N+1} mgx_i$$

The "walls" are two fixed particles at $x = 0$ and $x = L$ (see Fig. 1).

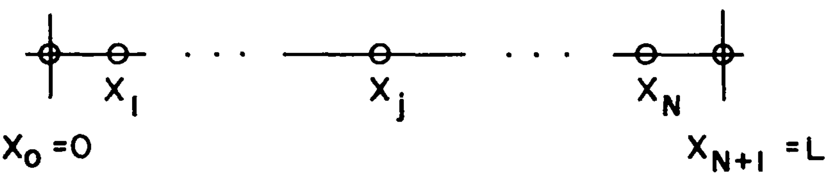

Figure 1. A system of N particles on a line of length L, with two fixed particles as walls.

The partition function $Q(N, L)$ for such a system is

$$Q(N, L) = \frac{\lambda^N}{N!} \int_0^L \cdots \int \exp\left[-\beta \sum_{i,j=0}^{N+1}{}' \phi(x_i - x_j) \right] \exp\left[- \sum_{i=1}^{N+1} bx_i \right] dx^N \tag{2.1}$$

in which the wall potentials have been included in the exponential, with

$$\lambda = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} \quad \text{and} \quad b = mg\beta$$

If the particles are ordered (we shall assume ϕ includes an impenetrable core) so that

$$0 \leqq x_1 \leqq x_2 \ldots \leqq x_{N-1} \leqq x_N \leqq L$$

(2.1) will become, because of the symmetry of the integral:

$$Q(N, L) = \lambda^N \int \cdots \int_{0 \leqq x_1 \leqq \ldots \leqq x_N \leqq L} \exp\left[-\beta \sum_{i=0}^{N} \phi(x_{i+1} - x_i) - \sum_{i=1}^{N+1} bx_i \right] dx^N \tag{2.2}$$

Calling $f(x) \equiv e^{-\beta\phi(x)}$ we have

$$Q(N, L) = \int_0^L dx_N \int_0^{x_N} dx_{N-1} \dots \int_0^{x_2} dx_1 f(x_1)$$
$$\times f(x_2 - x_1) \dots f(x_N - x_{N-1}) f(L - x_N)$$
$$\times e^{-bx_1} e^{-bx_2} \dots e^{-bx_N} e^{-bL} \tag{2.3}$$

Let us transform into difference coordinates:

$$y_1 = x_1,$$
$$y_2 = x_2 - x_1,$$
$$\vdots$$
$$y_N = x_N - x_{N-1},$$
$$y_{N+1} = L - x_N ;$$

so that we can write the Laplace transform (LT) of $Q(N, L)$,

$$\tilde{Q}(N, s) = \int_0^\infty e^{-sL} Q(N, L)\, dL$$
$$= \int_0^{\infty} \cdots \int f(y_1) f(y_2) \dots f(y_N) f(y_{N+1})$$
$$\times e^{-(s+b)y_{N+1}} e^{-(s+2b)y_N} \dots e^{-(s+Nb)y_2}$$
$$\times e^{-(s+(N+1)b)y_1}\, dy_1 \dots dy_{N+1}$$
$$= \prod_{j=1}^{N+1} \int_0^\infty f(y)\, e^{(bj+s)y}\, dy \tag{2.4}$$

Thus, if

$$\tilde{f}(s) = \int_0^\infty e^{-sy} f(y)\, dy$$

$$\tilde{Q}(N, s) = \prod_{j=1}^{N+1} \tilde{f}(s + bj) \tag{2.5a}$$

and

$$Q(N, L) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{sL} \prod_{j=1}^{N+1} \tilde{f}(s + bj)\, ds \tag{2.5b}$$

and the many body problem has been reduced to a single integration for any nearest neighbor potential.

When Eq. (2.5) is specialized to hard rods of diameter a:

$$\Phi(x) = 0 \qquad (x \geqq a)$$
$$= \infty \qquad (x < a),$$

so that

$$\tilde{f}(s+bj) = \frac{e^{-(bj+s)a}}{bj+s}$$

the inversion of the LT is easily performed by integrating over the contour shown in Fig. 2.

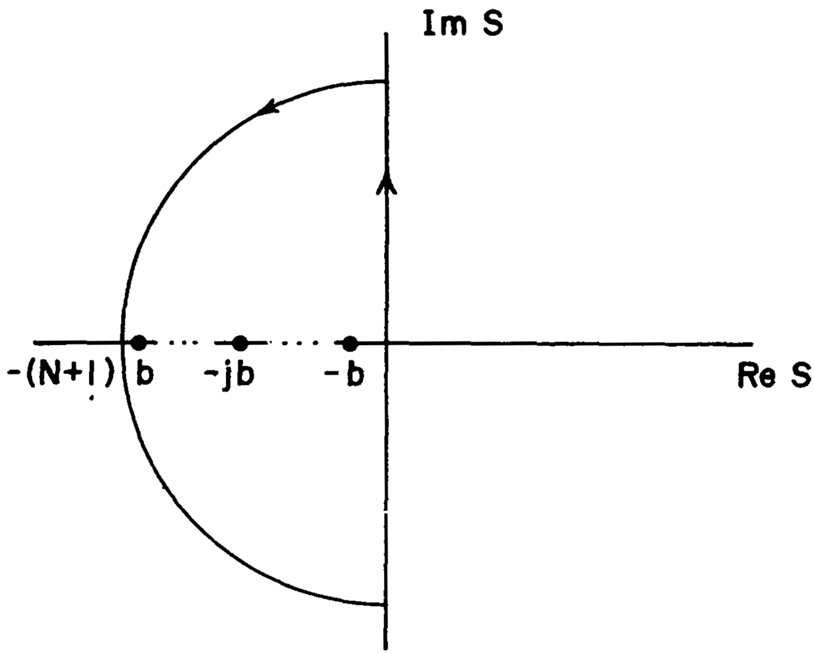

Figure 2. Contour of integration in Eq. (2.5b).

The result is

$$Q(N, L) = \frac{\lambda^N e^{-bL}}{N! b^N} e^{-baN(N+1)/2} \sum_{k=0}^{N} (-1)^k \binom{N}{k} e^{-b(L-(N+1)a)k}$$
$$= \frac{\lambda^N e^{-bL}}{b^N N!} e^{-baN(N+1)/2} \left(1 - e^{-b(L-(N+1)a)}\right)^N \tag{2.6}$$

3. Calculation of One- and Two-Particle Distribution Functions

The one-particle distribution $n(x)$ is given by the canonical average

$$\left\langle \sum_{i=1}^{N} \delta(x_i - x) \right\rangle$$

that is

$$n(x) = Q(N, L)^{-1} \times \frac{\lambda^N}{N!} \int_0^L \cdots \int \sum_{i=1}^{N} \delta(x_i - x)$$

$$\times \exp\left[-\beta \sum_{i,j=0}^{N+1}{}' \phi(x_i - x_j) - \sum_{i=1}^{N+1} bx_i \right] dx^N$$

$$= Q(N, L)^{-1} \int_{0 \leq x_1 \leq \ldots x_N \leq L} \cdots \int \sum_{i=1}^{N} \delta(x_i - x) \exp\left[-\beta \sum_{i=0}^{N} \phi(x_{i+1} - x_i) \right]$$

$$\times \exp\left(- \sum_{i=1}^{N+1} bx_i \right) dx^N \tag{3.1}$$

Now each δ-function creates a wall between left and right hand sides of the system so we can write

$$n(x) = \sum_{j=1}^{N} Q(j-1, x) Q(N-j, L-x) Q(N, L)^{-1} \tag{3.2}$$

In (3.2) $Q(0, x) = e^{-\beta\phi(x) - bx}$ and $Q(0, L-x) = e^{\beta\phi(L-x) - bL}$. Since $Q(j-1, x)$ is obtained from (2.6) with the replacement $N \to j-1$, $L \to x$ and $Q(N-j, L-x)$ is similarly obtained by $N \to N-j$, $L \to L-x$ (except that it contains an extra factor $e^{-bx(N-j+1)}$ due to the asymmetry of left and right hand sides of the system when expressed in difference coordinates), we will have

$$n(x) = \sum_{j=1}^{N}{}' bj \binom{N}{j} e^{-b(x-ja)(N-j+1)}$$

$$\times (1 - e^{-b(x-ja)})^{j-1} (1 - e^{-b(L-x-(N-j+1)a)})^{N-j} (1 - e^{-b(L-(N+1)a)})^{-N}, \tag{3.3}$$

in the region $a \leqslant x \leqslant L-a$ (it is of course zero elsewhere). The prime indicates that within the sum take $x \geqslant ja$.

We shall be interested mainly in the semi-finite system, approached as $L \to \infty$, with N large, but fixed. In that limit

$$n(x) = \sum_{j=1}^{N}{}' \, bj \binom{N}{j} e^{-(x-ja)(N-j+1)} (1 - e^{-b(x-ja)})^{j-1} \qquad (a \leqq x < \infty) \tag{3.4}$$

We record, for future reference, the LT of $n(x)$:

$$\begin{aligned} \tilde{n}(s) &= \int_0^1 (y + (1-y)\, e^{-as})^{N-1} y^{s/b} N e^{-as}\, dy \\ &= N e^{-aNs} \sum_{k=0}^{N-1} \binom{N-1}{k} \frac{(e^{as}-1)^k}{s/b+k+1} \end{aligned} \tag{3.5}$$

The two-particle distribution, $n_2(x, y)$, or the canonical average

$$\left\langle \sum_{\substack{i,j \\ i \neq j}}^{N} \delta(x_i - x)\delta(x_j - y) \right\rangle$$

is calculated in a similar fashion. If the ith particle is at x and the $i+j$th at y, $y > x$,

$$n_2(x, y) = \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \, Q(i-1, x) Q(j-1, y-x) Q(N-i-j, L-y)\, Q(N, L)^{-1} \tag{3.6}$$

with the sums subject to $i + j \leqslant N$

The result in the large L limit is:

$$\begin{aligned} n_2(x, y) = \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \, b^2 \frac{N!}{(i-1)!\,(j-1)!\,(N-i-j)!} e^{-b(x-ia)(N-i+1)} \\ \times e^{-b(y-x-ja)(N-i-j+1)} (1 - e^{-b(x-ia)})^{i-1} (1 - e^{-b(y-x-ja)})^{j-1} \end{aligned} \tag{3.7}$$

Inside the sum we take $x \geqq ia$ and $y - x \geqq ja$.

It is easy to calculate higher distributions by the same method.

4. Limiting Cases; Corrections to Barometric Density and Pressure

If we look at (3.3), which gives the one-particle distribution (density) for the finite system, we see that the initial density, i.e. at $x = a$ is

$$n(a) = \frac{bN}{(1 - e^{-b(L-(N+1)a)})}$$

which shows a volume exclusion term compared to the perfect gas. But in general (3.3) is not easily compared either to a free system or to a uniform hard rod fluid. We examine instead limiting cases, where either a, the hard rod diameter, or b, the external field strength is small.

If we have a nearly uniform fluid perturbed by a very weak gravitational field, we may approximate $n(x)$ by expanding (3.1) directly in powers of b:

$$n(x) = n^0(x) - bxn^0(x) - b\int_a^{L-a} [n_2^0(x,y) - n^0(x)n^0(y)]y\,dy + O(b^2)$$

$$(a \leqslant x \leqslant L-a) \qquad (4.1)$$

in which the "0" denotes pure hard rod distributions. Let us choose, N, L very large with $N/L = \rho$ (uniform density), and with x far from both walls ($x \gg 0$, $x \ll L$). Then (4.1) simplifies to

$$n(x) = \rho(1-bx) - b\rho^2\int_0^\infty (g^0(x-y)-1)y\,dy + O(b^2) \qquad (4.2)$$

or defining $G(x)\text{n} = n(x) - \rho$,

$$G(x) = -\rho bx - 2\rho^2 bx\int_0^\infty h^0(y)\,dy + O(b^2) \qquad (4.3)$$

with $h(x) \equiv g(x) - 1$.

Equation (4.3) has a rather limited region of validity, for the density becomes negative when x is sufficiently large. On the other hand x must be much larger than 0 if the effect of the wall particle on the density is to be neglected.

Interestingly, Eq. (4.3) results as well from the local density expansion of Lebowitz and Percus.[1] Using the grand canonical ensemble, they find, when the external field causes only slight inhomogeneities in the fluid,

$$\mu = U(x) + \mu^0(n(x)) \qquad (4.4)$$

where μ is the chemical potential of a system subject to an external potential $U(x)$ and $\mu_0(n(x))$ is the chemical potential of a *uniform* system which has constant density $n(x)$, (and is thus a function of x). Rewriting (4.4) in terms of $G(x)$ which we assume to be $\ll \rho$ and expanding through the term linear in $G(x)$ we have:

$$\mu - \mu^0(\rho + G(x)) \cong -\frac{\partial\mu^0(\rho)}{\partial\rho}\,G(x) = U(x) \qquad (4.5)$$

Since[2]

$$\rho \frac{\partial \mu^0}{\partial \rho} = \frac{\partial P}{\partial \rho} = \frac{1}{\beta}(1 + \rho \int h^0(x)\, dx)^{-1}$$

we have

$$G(x) = - \rho\beta U(x)\,(1 + 2\rho \int_0^\infty h^0(x)\, dx) \tag{4.6}$$

which agrees with (4.3) for gravitational potentials. It is curious that the Lebowitz–Percus expansion, which is much more useful in obtaining the asymptotic form of the uniform pair distribution than an expansion of the density in the potential, should simply reproduce the latter here.

More interesting is the limit of a non-uniform fluid of very small hard rods, i.e. the dimensionless constant ba is very small. From (3.4) or more simply from (3.5), we obtain in this limit (also $L \to \infty$),

$$n(x) = Nbe^{-bx} + [N^2be^{-bx} - 2N(N-1)be^{-2bx}]ba + O((ba)^2) \qquad (x > 0) \tag{4.7}$$

giving a first-order correction to the barometric density law.

The pressure of our system has two parts: a "kinetic" pressure which arises from the momentum transferred per unit time across a small surface S perpendicular to the line $(0, L)$ at x, and a "potential" pressure arising from the forces acting across this surface due to particles momentarily on opposite sides of it. The first of these, $P_k(x)$, is calculated as follows. The number of molecules crossing S at x with momentum p is $n(x,p)\, dx\, dp$. The total momentum transferred in unit time, allowing all possible values of p is then

$$\int_{-\infty}^{\infty} n(x,p) p^2\, dp$$

but since the momentum distribution is Maxwellian, the integration can be performed leaving

$$\beta P_k(x) = n(x). \tag{4.8}$$

The potential pressure, $P_\phi(x)$, or total force across S we find as follows. (See figure 3.) The force on particles near y due to a particle at z is

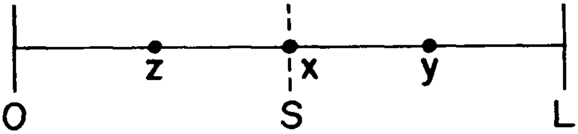

Figure 3. Distances for calculation of potential pressure.

$-n(y\,|\,z)\,d/dy\;\phi(y-z)\,dy$, where $n(y\,|\,z)$ is the (conditional) density at y in the presence of a particle at z, and is equal to $n_2(z,y)/n(z)$. Since there are $n(z)\,dz$ particles near z, the total force across S, and hence P_ϕ, is

$$P_\phi(x) = -\int_a^x\int_x^{L-a} n_2(z,y)\frac{d}{dy}\,\phi(y-z)\,dy\,dz \tag{4.9}$$

This vanishes at $x = a$, and $x = L-a$ so the wall particles do not contribute directly, but only through the pair distribution. When ϕ is the hard rod potential, it is easy to see that while $n_2(z,y)$ vanishes when $y-z = a$, $e^{+\beta\phi(y-z)}n_2(z,y) \equiv f(z,y)$ is continuous at $y-z = a$ just as it is for a uniform system. Thus,

$$\begin{aligned}
\beta P_\phi(x) &= \int_a^x\int_x^{L-a} f(z,y)\frac{d}{dy}(e^{-\beta\phi(y-z)})\,dy\,dz \\
&= \int_a^x\int_x^{L-a} f(z,y)\delta(y-z-a) \qquad dy\,dz \\
&= \begin{cases}
\displaystyle\int_a^x n_2(z,z+a)\,dz & (a < x < 2a) \\
\displaystyle\int_{x-a}^x n_2(z,z+a)\,dz & (2a < x < L-2a) \\
\displaystyle\int_{x-a}^{L-2a} n_2(z,z+a)\,dz & (L-2a < x < L-a)
\end{cases}
\end{aligned} \tag{4.10}$$

The derivation of the "potential" pressure given here avoids the approximation which is made in the usual derivation via the stress tensor. As a check on the correctness of (4.10) let x be far from the walls and remove the external potential. The pair distribution now depends only on the difference of its arguments and the correct uniform value, $a\rho^2 g(a)$ results.

Returning to the pressure calculation, the total pressure

$$P(x) = P_k(x) + P_\phi(x),$$

is obtained by adding (4.8) and (4.10). Taking the Laplace Transform in the large L limit,

$$B\tilde{P}(s) = \beta\int_a^\infty e^{-xs}P(x)\,dx = \tilde{n}(s) + \frac{1}{s}(1-e^{-as})\tilde{m}(s) \tag{4.11}$$

where

$$\tilde{m}(s) = \int_a^\infty e^{-xs} n_2(x, x+a)\, dx$$

This integral is similar in form to the density integral (3.5). To see this we employ (3.7),

$$n_2(x, x+a) = \sum_{i=1}^{N-1} b^2 iN \binom{N-1}{i} e^{-b(x-ia)(N-i+1)}(1-e^{-b(x-ia)})^{i-1} \tag{4.12}$$

so that

$$\tilde{m}(s) = bN(N-1)e^{-as} \int_0^1 (y+(1-y)e^{-as})^{N-2} y^{s/b+1}\, dy \tag{4.13}$$

Equation (4.11) with (3.5) and (4.13) is the exact pressure for any size hard rods.

Initially, at $x = a$ we have $\beta P(a) = n(a)$, but to characterize the pressure further we will proceed as we did with the density and examine the limit in which ba is small. In this limit the second term on the right in (4.11) becomes

$$a \,.\, \tilde{m}(s)]_{a=0} + O((ba)^2) = \frac{bN(N-1)}{s/b+2} ba + O((ba)^2)$$

Inverting, and employing (4.7)

$$\beta P(x) = Nbe^{-bx} + [N^2 be^{-bx} - N(N-1)be^{-2bx}]ba + O((ba)^2) \qquad (x > 0) \tag{4.14}$$

The bracketted term is positive showing the pressure increase due to the repulsive cores. Equations (4.7) and (4.14) are corrections to the familiar barometric density and pressure laws.

5. Discussion

We would like to indicate two directions for further study on this model and the mathematical difficulties encountered. First, we should be able to obtain an expansion for the logarithm of the grand partition function in powers of the activity z ($z = e^{\beta\mu}\lambda$) in which the "virial coefficients" are modifications of the reducible cluster integrals found in the theory of homogeneous imperfect gases.[3] These coefficients are explicitly known for pure hard rods,[4]

$$b_l = (-al)^{l-1}/l!.$$

Second, it would be of interest to study the distribution of zeros of the grand partition function in the complex z plane (or at least the limiting distribution, as $L \to \infty$). Again, this problem has been solved for pure hard rods.[5] The author knows of no example of either for an inhomogeneous continuum fluid. We indicate an approach to these questions. The grand partition function for the present system is

$$\mathfrak{Z}(z,L,\beta) = \sum_{N=0}^{N_{\max}} z^N Q(N,L) = \sum_{N=0}^{N_{\max}} \frac{z^N}{N!b^N} e^{-bL-[abN(N+1)/2]} \times (1 - e^{-b(L-(N+1)a)})^N$$

Taking $L/a = M$, to be the integer $N_{\max}$, we can rewrite (5.1) using the Cauchy integral theorem,

$$\mathfrak{Z}(z,M,\beta) = e^{-baM} \sum_{N=0}^{M} \left(\frac{2z}{b} e^{-baM/2}\right)^N \cdot \frac{1}{2\pi i} \int_C \exp\left[\lambda \sinh \frac{ba}{2}(M-N)\right] \frac{d\lambda}{\lambda^{N+1}} \tag{5.2}$$

The closed curve C encircles the origin in the complex λ plane. Further progress on either of the questions mentioned above depends on performing the sum in (5.2) which, so far, the author has been unable to do.

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