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Equilibrium State of a Classical Fluid of Hard Rods in an External Field

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The external field required to produce a given density pattern is obtained explicitly for a classical fluid of hard rods. All direct correlation functions are shown to be of finite range in all pairs of variables. The one-sided factors of the pair direct correlation are also found to be of finite range.

KEY WORDS: One-dimensional fluid; hard rods; nonuniform; direct correlation function.

1. INTRODUCTION

The study of the structure of nonuniform fluids is becoming an area of well-merited increasing activity (see, e.g., Ref. 1). One of the problems confronting attempts at effective approximation methods is the paucity of exactly solvable model systems which might serve as guides. One can say, largely after the event, that much of the progress made in classical uniform fluid structure has arisen from concepts which are most clearly presented in the context of a fluid of one-dimensional hard cores. In this paper we shall solve, essentially completely, the classical equilibrium statistical mechanics of a hard-rod fluid in an arbitrary external field. Our major conclusion will be that the short-range properties of the pair direct correlation function and its derived functions, which are crucial to analysis of the uniform fluid, remain valid in the presence of an external field. This suggests that approximations based upon these properties in realistic uniform fluids will remain suitable in the presence of nonuniformity.

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2. BASIC SOLUTION

We consider a system of hard rods—one-dimensional hard cores—of diameter a in an external potential $u(x)$ at reciprocal temperature β and fugacity z. Classical equilibrium statistical mechanics is then determined by the grand partition function, which may be written assuming that the integrals converge,

$$\Xi = \sum_0^\infty z^N \underset{\substack{x_1+a\le x_2 \\ \cdots \\ x_{N-1}+a\le x_N}}{\int\cdots\int} \exp\left[-\beta\sum_1^N u(x_i)\right] dx_N \cdots dx_1 \tag{1}$$

The various distribution functions arise from fixing appropriate integration variables, and so let us generalize (1) to the definition

$$\begin{aligned} \Xi(x, y) &= \sum_0^\infty z^N \underset{\substack{x+a\le x_1 \\ \cdots \\ x_N+a\le y}}{\int\cdots\int} \exp\left[-\beta\sum_1^N u(x_i)\right] dx_N \cdots dx_1 \\ &\qquad \text{for} \quad x + a \leqslant y \\ \Xi(x, y) &= 0 \qquad \text{for} \quad x + a > y \end{aligned} \tag{2}$$

Of course, then, $\Xi = \Xi(-\infty, \infty)$.

It is simplest to generate the system distribution functions by functional differentiation (see, e.g., Ref. 2). We have

$$\begin{aligned} \rho(x) &= \delta(\ln \Xi)/\delta - \beta u(x) \\ &= z e^{-\beta u(x)} \Xi(-\infty, x)\Xi(x, \infty)/\Xi \end{aligned} \tag{3}$$

$$\begin{aligned} \rho_2(x, y) &= e^{-\beta u(y)}\, \delta\rho(x) e^{\beta u(x)}/\delta - \beta u(y) \\ &= z^2 e^{-\beta u(x)} e^{-\beta u(y)} \Xi(-\infty, x)\Xi(x, y)\Xi(y, \infty)/\Xi, \qquad \text{for} \quad x \leqslant y \end{aligned} \tag{4}$$

To evaluate these, we must find $\Xi(x, y)$. But directly from the definition (2),

$$\begin{aligned} (\partial/\partial x)\Xi(x, y) &= -z e^{-\beta u(x+a)} \Xi(x + a, y) - \delta(x + a - y) \\ (\partial/\partial y)\Xi(x, y) &= z e^{-\beta u(y-a)} \Xi(x, y - a) + \delta(x + a - y) \end{aligned} \tag{5}$$

which may be solved explicitly in special cases. A change of viewpoint is, however, helpful. To emphasize that the problem lies in the nonuniformity of the system, we will express all distributions in terms of $\rho(x)$ rather than of $u(x)$. Thus we must first solve for u in terms of ρ.

Reduced to the quantities entering into $\rho(x)$, (5) tells us that

$$\begin{aligned} (\partial/\partial x)\Xi(x, \infty) &= -z e^{-\beta u(x+a)} \Xi(x + a, \infty) \\ (\partial/\partial x)\Xi(-\infty, x) &= z e^{\beta u(x-a)} \Xi(-\infty, x - a) \end{aligned} \tag{6}$$

and hence

$$\begin{aligned}(\partial/\partial x)\Xi(x, \infty) &= -\Xi\rho(x + a)/\Xi(-\infty, x + a)\\ (\partial/\partial x)\Xi(-\infty, x) &= \Xi\rho(x - a)/\Xi(x - a, \infty)\end{aligned} \tag{7}$$

It follows that $(\partial/\partial x)[\Xi(x - a, \infty)\Xi(-\infty, x)] = \Xi(\rho(x - a) - \rho(x))$, or

$$\Xi(x - a, \infty)\Xi(-\infty, x) = \left(C - \int_{x-a}^{x} \rho(z)\, dz\right)\Xi \tag{8}$$

for a suitable constant C. Assume that $\rho(x) \to 0$ as $x \to \pm\infty$. Then, letting $x \to \infty$ in (8), $1 \cdot \Xi = \Xi \cdot C$ or $C = 1$. Now

$$(\partial/\partial x)\Xi(x, \infty) = -\rho(x + a)\Xi(x, \infty)\Big/\left[1 - \int_{x}^{x+a} \rho(w)\, dw\right]$$

so that, using the boundary condition as $x \to \infty$,

$$\Xi(x, \infty) = \exp + \int_{x}^{\infty} \frac{\rho(z + a)}{1 - \int_{x}^{z+a} \rho(w)\, dw}\, dz \tag{9}$$

Similarly

$$\Xi(-\infty, x) = \exp \int_{-\infty}^{x} \frac{\rho(z - a)}{1 - \int_{z-a}^{z} \rho(w)\, dw}\, dz \tag{10}$$

and of course

$$\Xi = \exp \int_{-\infty}^{\infty} \frac{\rho(z - a)}{1 - \int_{z-a}^{z} \rho(w)\, dw}\, dz \tag{11}$$

Inserting (9)–(11), we therefore have from (3) the desired u–ρ relation

$$\beta u(x) + \ln \rho(x) - \ln z = \int_{-\infty}^{x} \left[\frac{\rho(z - a)}{1 - \int_{z-a}^{z} \rho(w)\, dw} - \frac{\rho(z + a)}{1 - \int_{z}^{z+a} \rho(w)\, dw}\right] dz \tag{12}$$

The right-hand side of (12) is readily transformed to

$$\int_{-\infty}^{x} \left[\frac{\rho(z)}{1 - \int_{z-a}^{z} \rho(w)\, dw} - \frac{\rho(z + a)}{1 - \int_{z}^{z+a} \rho(w)\, dw}\right] dz + \ln\left[1 - \int_{x-a}^{x} \rho(w)\, dw\right]$$

thereby yielding the local form

$$\begin{aligned}\beta u(x) + \ln \rho(x) - \ln z = {}& \ln\left[1 - \int_{x-a}^{x} \rho(w)\, dw\right]\\ & - \int_{x}^{x+a} \frac{\rho(z)}{1 - \int_{z-a}^{z} \rho(w)\, dw}\, dz\end{aligned} \tag{13}$$

3. DISTRIBUTION FUNCTIONS

The modifications of the bulk properties of the core system due to an imposed field are now quite easy to assess. Let us look first at the pair distribution, or, for somewhat easier interpretation, the conditional density at y due to a particle known to be at $x < y$. We have from (3) and (4)

$$\rho(y|x) = \rho_2(x, y)/\rho(x) = \Xi(x, y)ze^{-\beta u(y)}\Xi(y, \infty)/\Xi(x, \infty) \tag{14}$$

Inserting (2) and (9), this may be written as

$$\rho(y|x) = \sum_1^\infty T^N(x, y) \tag{15a}$$

where

$$T(x, y) \equiv \epsilon(y - x - a)z \exp - \left[\beta u(y) + \int_x^y \frac{\rho(z + a)}{1 - \int_z^{z+a} \rho(w)\, dw}\, dz\right] \tag{15b}$$

$$\begin{aligned} \epsilon(x) &= 1 \qquad \text{for} \quad x \geqslant 0 \\ &= 0 \qquad \text{for} \quad x < 0 \end{aligned}$$

Equation (15) is in fact a decomposition of the conditional density into layers, familiar from the uniform fluid case (see, e.g., Ref. 3). The Nth term contributes when the particle at y is the Nth neighbor of that at x. The chain of N particles is a Markov chain with transition matrix $T(x, y)$, which contains the core exclusion, the expected Boltzmann factor due to the external u, as well as a Boltzmann factor due to the pressure field to the right of y. The effective pressure is clearly given by

$$\beta P(y) = (d/dy)\int_x^y \rho(z + a)\, dz \Big/ \left[1 - \int_z^{z+a} \rho(w)\, dw\right]$$

or

$$\beta P(y) = \rho(y + a) \Big/ \left[1 - \int_y^{y+a} \rho(w)\, dw\right] \tag{16}$$

This will be recognized as the hard-core equation of state in which the numerator or transport part uses the contact density at the interface of a particle at y with the fluid to the right, while the denominator uses the mean density between particle and interface.

From the viewpoint of analytic simplicity, it is far easier and equally significant to obtain the sequence of inverse or so-called direct correlation functions. These may be defined by[2]

$$c_s(x_1, \ldots, x_s) = \frac{\delta^{s-1}}{\delta\rho(x_2) \cdots \delta\rho(x_s)} [\beta u(x_1) + \ln \rho(x_1)] \tag{17}$$

In particular, for the basic pair direct correlation $c_2(x, y)$, we have at once from (13)

$$c_2(x, y) = \frac{-\epsilon(x - y)\epsilon(y - x + a)}{1 - \int_{x-a}^{x} \rho(w)\,dw} - \frac{\epsilon(y - x)\epsilon(x - y + a)}{1 - \int_{y-a}^{y} \rho(w)\,dw} - \int \frac{\rho(z)\epsilon(z - x)\epsilon(x + a - z)\epsilon(z - y)\epsilon(y + a - z)}{\left[1 - \int_{z-a}^{z} \rho(w)\,dw\right]^2}\,dz \tag{18}$$

perhaps more transparent in the form

$$c_2(x, y) = \frac{-1}{1 - \int_{y-a}^{y} \rho(w)\,dw} - \int_{y}^{x+a} \frac{\rho(z)\,dz}{\left[1 - \int_{z-a}^{z} \rho(w)\,dw\right]^2} \tag{19}$$

when $x \leqslant y \leqslant x + a$. The important thing to notice about (18) is that c_2 has precisely the range of the hard core: $c_2(x, y) = 0$ unless $|x - y| \leqslant a$. The Ornstein–Zernicke,[4] Percus–Yevick,[5] hard-core insertion,[6] or generalized mean spherical model[7] approximation that c_2 vanishes outside the range of interaction holds exactly for rods in an external field.

The full sequence of c_s is no harder to obtain. Repeatedly using

$$\frac{\delta}{\delta\rho(x)} \int_{y-a}^{y} \rho(w)\,dw = \epsilon(y - x)\epsilon(x - y + a) \tag{20}$$

we find at once from (17)

$$\frac{c_s(x_1, \ldots, x_s)}{(s - 2)!} = -\sum_{i=1}^{s} \frac{\prod_{j \neq i} [\epsilon(x_i - x_j)\epsilon(x_j - x_i + a)]}{\left[1 - \int_{x_i-a}^{x_i} \rho(w)\,dw\right]^{s-1}} - (s - 1) \int \frac{\rho(z) \prod_{j=1}^{s} [\epsilon(z - x_j)\epsilon(x_j - z + a)]}{\left[1 - \int_{z-a}^{z} \rho(w)\,dw\right]^{s}}\,dz \tag{21}$$

and conclude that in fact c_s is of range a in each pair of coordinates. Another consequence of (21) is that c_s is negative at every point in s-space on its non-vanishing domain.

4. FURTHER PROPERTIES OF THE PAIR DIRECT CORRELATION

The original Ornstein–Zernike definition[4] of the pair direct correlation, equivalent to (17), is that, matrixwise,

$$C = S^{-1} \tag{22}$$

where

$$C(x, y) = \delta(x - y)/\rho(y) - c_2(x, y) \tag{23}$$

and $S(x, y)$ is the modified pair Ursell function

$$\begin{aligned} S(x, y) &= \langle [\hat{\rho}(x) - \rho(x)][\hat{\rho}(y) - \rho(y)] \rangle \\ &= \rho(x)\,\delta(x - y) + F(x, y) \\ &= \rho(x)\,\delta(x - y) + \rho_2(x, y) - \rho(x)\rho(y) \end{aligned} \tag{24}$$

Here $\hat{\rho}(x)$ is the instantaneous microscopic density $\sum_i \delta(x - x_i)$. Clearly $S(x, y)$ is positive definite, so that (if S is bounded) $C(x, y)$ is positive definite as well. It is then always possible to write[2]

$$C = (I - Q\rho)\rho^{-1}(I - \rho Q^{+}) \tag{25}$$

for suitable Q, where $\rho(x, y) \equiv \rho(x)\,\delta(x - y)$. We shall investigate the properties of the matrix Q.

Of course Q is not determined uniquely by (25). It becomes so to within a diagonal multiplier if we impose the condition $Q(x, y) \neq 0$ only for $x \geqslant y$, so that $Q^{+}(x, y) \neq 0$ only for $x \leqslant y$. For a uniform hard-rod system, it is known[8] that Q, so restricted, is of range a as well. Let us assume that here, too, we have

$$\begin{aligned} Q^{+}(x, y) &\neq 0 \qquad \text{only for} \quad x \leqslant y \leqslant x + a \\ Q(x, y) &\neq 0 \qquad \text{only for} \quad x - a \leqslant y \leqslant x \end{aligned} \tag{26}$$

certainly implying that c_2 is of range a. We will now verify this supposition, determine Q, and incidentally quickly rederive the result (18).

According to (22), (24), and (25), $I = (I - Q\rho)\rho^{-1}(I - \rho Q^{+})(\rho + F)$. Hence $(I - \rho Q^{+})(\rho + F) = \rho(I - Q\rho)^{-1}$, or

$$F - \rho Q^{+}\rho - \rho Q^{+}F = \rho Q\rho(I - Q\rho)^{-1} \tag{27}$$

and explicitly

$$\begin{aligned} F(x, y) - \rho(x)\rho(y)Q^{+}(x, y) - \rho(x)\int Q^{+}(x, z)F(z, y)\,dz \\ = \rho(x)\sum_{1}^{\infty}(Q\rho)^{j}(x, y) \end{aligned} \tag{28}$$

The information we have available is that, while Q and Q^{+} are short range, $\rho_2(x, y)$ has no short-range part: $\rho_2(x, y) = 0$ for $|x - y| \leqslant a$, or

$$F(x, y) = -\rho(x)\rho(y) \qquad \text{for} \quad |x - y| \leqslant a \tag{29}$$

Now consider (28) in the domain $x \leqslant y \leqslant x + a$; there it reduces to

$$-\rho(x)\rho(y) - \rho(x)\rho(y)Q^{+}(x, y) - \rho(x)\rho(y)\int_{x}^{x+a} Q^{+}(x, z)\rho(z)\,dz = 0$$

[2] For uniform systems, see Ref. 8.

or to

$$Q^+(x, y) = -1 - \int_x^{x+a} Q^+(x, z)\rho(z)\, dz \qquad \text{for} \quad x \leqslant y \leqslant x + a \quad (30)$$

The solution of (30) is straightforward. We have

$$\int_x^{x+a} Q^+(x, y)\rho(y)\, dy = -\int_x^{x+a} \rho(y)\, dy \left[1 + \int_x^{x+a} Q^+(x, z)\rho(z)\, dz\right]$$

Solving for $\int_x^{x+a} Q^+(x, y)\rho(y)\, dy$ and inserting in (30) in the region $x \leqslant y \leqslant x + a$, it follows that

$$Q^+(x, y) = -\epsilon(y - x)\epsilon(x - y + a)\Big/\left[1 - \int_x^{x+a} \rho(z)\, dz\right] \qquad (31)$$

whence

$$Q(x, y) = -\epsilon(x - y)\epsilon(y - x + a)\Big/\left[1 - \int_y^{y+a} \rho(z)\, dz\right] \qquad (32)$$

Now if (31) and (32) are substituted into (25) in the form [see (23)]

$$c_2 = Q + Q^+ - Q\rho Q^+ \qquad (33)$$

(18) is precisely reproduced. Thus the assumption (26) is validated, and yet another aspect of bulk system distributions is maintained in the face of nonuniformity.

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