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One-Dimensional Classical Fluid with Nearest-Neighbor Interaction in Arbitrary External Field

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We consider the equilibrium statistical mechanics of a classical one-dimensional simple fluid, with nearest-neighbor interactions, and in an arbitrary external potential. The external potential is eliminated to yield relations between the truncated partition functions and the one-body density. These relations are solved for pure cores and for sticky cores, resulting in each case in both an explicit potential density relation and grand potential density functional. Both models maintain finite-range direct correlations and have grand potentials expressible in terms of simple linear density transforms.

KEY WORDS: One-dimensional; nonuniform; classical fluid; sticky cores.

1. INTRODUCTION

The microscopic structure of a classical fluid in thermal equilibrium has been investigated in ever-increasing detail. Qualitative characteristics of uniform system distribution functions are well understood, including those in the important critical region. The situation for nonuniform fluids is less clear, with a certain amount of controversy still present,[1] and even empirical methods for determining microscopic structure leave something to be desired. Under these circumstances, examination of model systems plays a useful role, allowing approximation methods to be evaluated, and suggesting others. The somewhat trivial simple (no internal degrees of freedom) one-dimensional fluid models thus become worth examining if

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they can be fully and explicitly analyzed. The important characteristic, and the major source of difficulty, is that this must be done in the context of an arbitrary fluid density pattern, obtained by the imposition of an arbitrary external field.

One such model, that in which the pair interaction potential is of pure hard core type, has previously been solved,[2] leading to a firmer appreciation of the merits of typical approximation methods, and suggesting[3] fairly simple three-dimensional model free energies as well. In this paper, we will investigate the extended class of one-dimensional fluids in which the nearest-neighbor nature of the interaction is retained, without at first making any further assumptions as to its form. Nearest-neighbor interaction of course corresponds to a real pair potential when the latter consists of a hard core followed by a tail of range less than that of the core. The key to the solution lies in the evaluation of the external potential required to produce a given density pattern, rather than the more customary reverse problem. After setting up the formal solution in this fashion, we will apply it to two specific models and then comment on the suggested implications for the structure of real fluids.

2. PARTITION FUNCTION FRAGMENTS

We have in mind a one-dimensional fluid, on the full line $-\infty < x < \infty$, with fixed interparticle potential $\phi(r - r')$ but arbitrary external potential $u(r)$. In this one-dimensional case, we can order N particles once and for all: $x_1 \leqslant x_2 \leqslant x_3 \ldots \leqslant x_N$ and compensate by including a permutation weight of $N!$. Here the order will be imposed by truncating the pair Boltzmann factor; we hence define

$$e(x,x') = \begin{cases} e^{-\beta\phi(x-x')}, & x \geqslant x' \\ 0, & x \leqslant x' \end{cases} \tag{2.1}$$

where $\beta = 1/kT$. Assuming nearest-neighbor interaction, the (momentum-integrated) canonical partition function thus becomes

$$Q_N = \int \cdots \int \prod_{i=2}^{N} e(x_i, x_{i-1}) \prod_{i=1}^{N} W(x_i) \prod_{i=1}^{N} dx_i \tag{2.2}$$

where $W(x) = e^{-\beta u(x)}$. Q_N exists if $W(x) \to 0$ sufficiently rapidly as $x \to \pm\infty$. We will be mainly concerned with the grand canonical partition function

$$\Xi_\mu = \sum_{N=0}^{\infty} e^{N\beta\mu} Q_N \tag{2.3}$$

and its consequences.

In order to introduce the relevant distribution functions, we first define the left and right fragments

$$Q_N(x) \equiv \int \cdots \int e(x, x_N) \prod_{i=2}^{N} e(x_i, x_{i-1}) \prod_{i=1}^{N} W(x_i) \prod_{i=1}^{N} dx_i$$

$$\hat{Q}_N(x) \equiv \int \cdots \int \prod_{i=2}^{N} e(x_i, x_{i-1}) \prod_{i=1}^{N} W(x_i) e(x_1, x) \prod_{i=1}^{N} dx_i \qquad (2.4)$$

$$Q_0(x) = \hat{Q}_0(x) = 1$$

in terms of which the canonical one-body distribution is given by

$$n_N(x)\, Q_N = W(x) \sum_{j=1}^{N} Q_{N-j}(x) \hat{Q}_{j-1}(x) \qquad (2.5)$$

Similarly, we define

$$\Xi_\mu(x) = \sum_0^\infty e^{N\beta\mu} Q_N(x)$$

$$\hat{\Xi}_\mu(x) = \sum_0^\infty e^{N\beta\mu} \hat{Q}_N(x) \qquad (2.6)$$

in terms of which

$$n(x) = w(x) \Xi(x) \hat{\Xi}(x) / \Xi_T \qquad (2.7)$$

where

$$w(x) = e^{\beta[\mu - u(x)]}$$

Here the chemical potential μ is understood, but to avoid later confusion we have written Ξ_T for the total grand partition formation.

Formally, there is little difficulty in solving for Ξ and $\hat{\Xi}$. We note from (2.4) that

$$Q_N(x) = \int e(x, x') W(x') Q_{N-1}(x')\, dx'$$

$$\hat{Q}_N(x) = \int e(x', x) W(x') \hat{Q}_{N-1}(x')\, dx' \qquad (2.8)$$

Hence if the continuous matrix with elements $e(x, x')$ is denoted by e, its adjoint by e^*, W is taken as a diagonal matrix, and Q, $\hat{Q}$ as the corresponding (column) vectors, we have

$$Q_N = eWQ_{N-1}$$

$$\hat{Q}_N = e^* W \hat{Q}_{N-1} \qquad (2.9)$$

From (2.6), then

$$\begin{aligned} \Xi &= ew\Xi + 1 \\ \hat{\Xi} &= e^* w\hat{\Xi} + 1 \end{aligned} \tag{2.10}$$

where 1 is the vector of all 1's, with immediate solution

$$\begin{aligned} \Xi &= (I - ew)^{-1}1 \\ \hat{\Xi} &= (I - e^*w)^{-1}1 \end{aligned} \tag{2.11}$$

The profile then follows from (2.7).

3. SOLUTION OF THE INVERSE PROBLEM

Equations (2.11) are not very helpful when explicit solutions are required for general w, and these indeed are not available in ordinary closed form. But implicit solutions are, in which w is expressed as a functional of the density. The strategy involves first eliminating w in favor of Ξ and $\hat{\Xi}$, obtaining these as functionals of the density, and then recovering $w[n]$.

We start by eliminating w between (2.7) and each of (2.10). This yields, with argument suppression,

$$\begin{aligned} \Xi &= e\left(\frac{n}{\hat{\Xi}}\right)\Xi_T + 1 \\ \hat{\Xi} &= e^*\left(\frac{n}{\Xi}\right)\Xi_T + 1 \end{aligned} \tag{3.1}$$

It is then convenient to assume (it will be true in our applications) that the inverses to e and e^*, in the sense that $e^{-1}e = I$, $(e^*)^{-1}e^* = I$, satisfy

$$e1 = e^*1 = 0 \tag{3.2}$$

Thus (3.1) becomes

$$n/\hat{\Xi} = e^{-1}\Xi/\Xi_T, \qquad n/\Xi = e^{*-1}\hat{\Xi}/\Xi_T \tag{3.3}$$

We then combine (3.3): $n/\Xi = e^{*-1}[n/(e^{-1}\Xi/\Xi_T)]/\Xi_T$, and similarly $n/\hat{\Xi} = e^{-1}[n/(e^{*-1}\hat{\Xi}/\Xi_T)]/\Xi_T$, so that

$$\begin{aligned} \frac{n(x)}{\Xi(x)} &= e^{*-1}\left[\frac{n(x)}{e^{-1}\Xi(x)}\right] \\ \frac{n(x)}{\hat{\Xi}(x)} &= e^{-1}\left[\frac{n(x)}{e^{*-1}\hat{\Xi}(x)}\right] \end{aligned} \tag{3.4}$$

our basic relation.

The elimination of 1 in (3.1) corresponds to the elimination of needed boundary conditions in (3.4). These can be recovered by returning to the original (2.10). We first recall for future use that

$$\Xi(\infty)=\hat{\Xi}(-\infty)=\Xi_T \tag{3.5}$$

On the other hand, from (2.10) it also follows that

$$\Xi(-\infty)=\hat{\Xi}(\infty)=1 \tag{3.6}$$

This is not sufficient. But reinserting (3.6) in (2.11), using the one-sided property of $e(x,x')$ and the conditions (3, 5),

$$\begin{aligned} \Xi(x)-1 &\to en(x) \qquad \text{as } x\to-\infty \\ \hat{\Xi}(x)-1 &\to e^*n(x) \qquad \text{as } x\to\infty \end{aligned} \tag{3.7}$$

which will suffice for uniqueness. Of course, once Ξ and $\hat{\Xi}$ have been determined as functionals of the density, the inverse profile–potential relation is simply (2.7), written as

$$w(x)=\frac{n(x)}{\Xi(x)\hat{\Xi}(x)}\,\Xi_T \tag{3.8}$$

Finally, we can put (3.4) into a superficially more general but actually more useful form. For this purpose, we introduce modified partition function fragments defined by

$$\Xi=\tau\Lambda,\qquad \hat{\Xi}=\tau^*\hat{\Lambda} \tag{3.9}$$

for suitable operator τ. Applying τ^* and τ to (3.4), we then have

$$\begin{aligned} \tau^*\left[\frac{n(x)}{\tau\Lambda(x)}\right] &= (e^{-1}\tau)^*\left[\frac{n(x)}{e^{-1}\tau\Lambda(x)}\right] \\ \tau\left[\frac{n(x)}{\tau^*\hat{\Lambda}(x)}\right] &= \tau e^{-1}\left[\frac{n(x)}{(\tau e^{-1})^*\hat{\Lambda}(x)}\right] \end{aligned} \tag{3.10}$$

the desired form. The important asymptotic conditions (3.7) then transcribe to

$$\begin{aligned} e^{-1}\tau\Lambda(x) &\to n(x) \qquad \text{as } x\to-\infty \\ (\tau e^{-1})^*\hat{\Lambda}(x) &\to n(x) \qquad \text{as } x\to\infty \end{aligned} \tag{3.11}$$

It may seem strange that it is necessary to introduce the right fragment, left fragment decomposition in order, e.g., to find Ξ_T. Indeed, it is not, and the original derivation used a somewhat less transparent technique[4] which avoided this decomposition. To gild a somewhat undistinguished lily, this derivation is presented in the Appendix.

4. PURE HARD-CORE FLUID

Our first application is to a previously solved problem.[2] Consider a hard-core interaction with core diameter a:

$$e(x,x') = \begin{cases} 1, & x - x' \geqslant a \\ 0, & x - x' < a \end{cases} \tag{4.1}$$

Since $e^{-1}(x,x') = \delta'(x - x' + a)$, then

$$\begin{aligned} e^{-1}f(x) &= f'(x+a) \\ e^{*-1}f(x) &= -f'(x-a) \end{aligned} \tag{4.2}$$

Equations (3.4) now become

$$\begin{aligned} n(x) &= -\Xi(x)\frac{d}{dx}\frac{n(x-a)}{\Xi'(x)} \\ n(x) &= -\hat{\Xi}(x)\frac{d}{dx}\frac{n(x+a)}{\hat{\Xi}'(x)} \end{aligned} \tag{4.3}$$

The first of (4.3), written as

$$n(x) = n(x-a) - \frac{d}{dx}\left[\frac{\Xi(x)}{\Xi'(x)}n(x-a)\right]$$

has the solution

$$\frac{\Xi(x)}{\Xi'(x)}n(x-a) = c_1 - \int_{x-a}^{x} n(y)\,dy \tag{4.4}$$

According to (3.7),

$$\ln\Xi(x) \to \int_{-\infty}^{x-a} n(y)\,dy \quad \text{or} \quad \Xi'(x)/\Xi(x) \to n(x-a) \qquad \text{as} \quad x \to -\infty$$

Hence $c_1 = 1$ in (4.4), which integrates to

$$\ln\Xi(x) = \int_{-\infty}^{x} \frac{n(z-a)}{1 - \int_{z-a}^{z} n(y)\,dy}\,dy \tag{4.5}$$

In just the same way, we find

$$\ln\hat{\Xi}(x) = \int_{x}^{\infty} \frac{n(z+a)}{1 - \int_{z}^{z+a} n(y)\,dy}\,dy \tag{4.6}$$

An immediate consequence of (4.5), or (4.6), is that

$$\Xi_T = \exp\int_{-\infty}^{\infty} \frac{n(z+a)}{1 + \int_{z}^{z+a} n(y)\,dy}\,dz \tag{4.7}$$

and a more detailed consequence, from (3.8), that

$$\beta(\mu - u(x)) = \ln n(x) - \int_{-\infty}^{x} \frac{n(z-a)}{1 - \int_{z-a}^{z} n(y)\,dy}\,dz + \int_{-\infty}^{x} \frac{n(z+a)}{1 - \int_{z}^{z+a} n(y)\,dy}\,dz \tag{4.8}$$

readily transformed to the local form

$$\beta(\mu - u(x)) = \ln\left\{ n(x) \Big/ \left[1 - \int_{x}^{x+a} n(y)\,dy\right]\right\} + \int_{x-a}^{x} \frac{n(z)}{1 - \int_{z}^{z+a} n(y)\,dy}\,dy \tag{4.9}$$

Equations (4.5)–(4.9) reproduce those found previously.

5. STICKY-CORE FLUID

To impart some vestige of realism to the interaction ϕ, we must at least include an attractive component. We can imagine this as softening the edge of the core and introducing an additional attractive tail:

$$e(x,x') = e_0(x - x' - a) + \Delta(x - x' - a) \tag{5.1}$$

where

$$\Delta(x) = e^{-\beta\phi(x+a)} - e_0(x)$$

Here e_0 is the Heaviside step function and Δ is of range less than a. Formally, we can then carry out a moment expansion of Δ:

$$\Delta(x) = \int \delta(x-y)\,\Delta(y)\,dy = \sum_{0}^{\infty} (-1)^s/s!\,\delta^{(s)}(x) \int y^s \Delta(y)\,dy$$

so that

$$e(x,x') = e_0(x - x' - a) + \sum_{0}^{\infty} \gamma_s\,\delta^{(s)}(x - x' - a) \tag{5.2}$$

where

$$\gamma_s = (-1)^s/s! \int y^s\,\Delta(y)\,dy.$$

In operator form, this reads

$$e = \Gamma(D) e_0 \tag{5.3}$$

where

$$\Gamma(D) = 1 + \sum_{0}^{\infty} \gamma_0 D^{s+1}, \qquad D \equiv \partial/\partial x$$

and similarly

$$e^* = \Gamma(-D)e_0^* \tag{5.4}$$

A convenient choice of τ in the context of (5.3) and (5.4) is simply $\tau = \Gamma(D)$. Then $e^{-1}\tau = e_0^{-1} = \tau e^{-1}$ on well-behaved functions, and (3.10) takes the form

$$\Gamma(-D)\left[\frac{n(x)}{\Gamma(D)\Lambda(x)}\right] = -\frac{d}{dx}\left[\frac{n(x-a)}{\Lambda'(x)}\right] \tag{5.5a}$$

$$\Gamma(D)\left[\frac{n(x)}{\Gamma(-D)\hat{\Lambda}(x)}\right] = -\frac{d}{dx}\left[\frac{n(x+a)}{\hat{\Lambda}'(x)}\right] \tag{5.5b}$$

where

$$\Xi = \Gamma(D)\Lambda, \qquad \hat{\Xi} = \Gamma(-D)\hat{\Lambda} \tag{5.5c}$$

It is not strictly necessary to solve for both Λ and $\hat{\Lambda}$, since it follows from definition, or from the equations (5.5) when each solution is unique, that

$$\hat{\Lambda}(x \mid n(y)) = \hat{\Lambda}(-x \mid n(-y)) \tag{5.6}$$

Consider then the first of (5.5). We can reduce the differential order by 1 by constructing the familiar bilinear concomitant[5]:

$$\begin{aligned} &\Lambda(x)\Gamma(-D)[n(x)/\Gamma(D)\Lambda(x)] \\ &\quad = \Gamma(D)\Lambda(x)[n(x)/\Gamma(D)\Lambda(x)] \\ &\quad\quad -(D_1+D_2)[\Gamma(D_1)-\Gamma(-D_2)/D_1-(-D_2)] \\ &\quad\quad \times[\Lambda(x)][n(x)/\Gamma(D)\Lambda(x)] \end{aligned}$$

where D_1 operates on the first of the parenthesized factors, D_2 on the second, or

$$\begin{aligned} \Lambda(x)\Gamma(-D)\left[\frac{n(x)}{\Gamma(D)\Lambda(x)}\right] &= n(x) - \frac{d}{dx}\,\frac{\Gamma(D_1)-\Gamma(-D_2)}{D_1+D_2} \\ &\quad \times[\Lambda(x)]\left[\frac{n(x)}{\Gamma(D)\Lambda(x)}\right] \end{aligned} \tag{5.7}$$

Applying (5.7) to both sides of (5.5a) and integrating, then

$$\begin{aligned} &n(x-a)\frac{\Lambda(x)}{\Lambda'(x)} - \frac{\Gamma(D_1)-\Gamma(-D_2)}{D_1+D_2}[\Lambda(x)]\left[\frac{n(x)}{\Gamma(D)\Lambda(x)}\right] \\ &\quad = c_1 - \int_{x-a}^{x} n(y)\,dy \end{aligned} \tag{5.8}$$

From (3.11), as $x \to -\infty$, $e^{-1}\tau\Lambda(x) = e_0^{-1}\Lambda(x) = \Lambda'(x+a)$, and from (3.5), $\Lambda(x) = \Xi(x) - \{[\Gamma(D) - 1]/D\}\Lambda'(x) \to 1$. Hence $c_1 = 1$ in (5.8).

Further reduction of (5.8) is not trivial, but it can be applied as it stands to the $s = 0$ version

$$\Gamma(D) = 1 + \gamma D \tag{5.9}$$

corresponding to the "sticky-core" model introduced by Baxter[6]

$$e(x, x') = e_0(x - x' - a) + \gamma\delta(x - x' - a) \tag{5.10}$$

in which the interaction is compressed to a 0-range attractive tail

$$\phi_A(x - x') = \lim_{\lambda \to 0} -\frac{1}{\beta}\left[e_0(x - x' - a) - e_0(x - x' - a - \lambda)\right]\ln\left(1 + \frac{\gamma}{\lambda}\right) \tag{5.11}$$

In this case, (5.8) specializes to

$$n(x-a)\frac{\Lambda(x)}{\Lambda'(x)} - \gamma\frac{n(x)\Lambda(x)}{\Lambda(x) + \gamma\Lambda'(x)} = 1 - \int_{x-a}^{x} n(y)\,dy \tag{5.12}$$

and the solution of the resulting quadratic equation that approaches zero as $n \to 0$ is

$$\begin{aligned}\Lambda'(x)/\Lambda(x) &= K(x)\\ &= \frac{1}{2\gamma}\left\{\left[\left(1 + \gamma\frac{n(x) - n(x-a)}{1 - \int_{x-a}^{x} n(y)\,dy}\right)^2 + \frac{4\gamma n(x-a)}{1 - \int_{x-a}^{x} n(y)\,dy}\right]^{1/2}\right.\\ &\qquad \left. - \left(1 + \gamma\frac{n(x) - n(x-a)}{1 - \int_{x-a}^{x} n(y)\,dy}\right)\right\}\end{aligned} \tag{5.13}$$

We conclude that

$$\Lambda(x) = \exp\int_{-\infty}^{x} K(z)\,dz \tag{5.14}$$

and similarly, directly from (5.6) that

$$\hat{\Lambda}(x) = \exp\int_{x}^{\infty} \hat{K}(z)\,dz$$

where

$$\begin{aligned}\hat{K}(x) &= \frac{1}{2\gamma}\left\{\left[\left(1 - \gamma\frac{n(x+a) - n(x)}{1 - \int_{x}^{x+a} n(y)\,dy}\right)^2 + \frac{4n(x+a)\gamma}{1 - \int_{x}^{x+a} n(y)\,dy}\right]^{1/2}\right.\\ &\qquad \left. - \left(1 - \gamma\frac{n(x+a) - n(x)}{1 - \int_{x}^{x+a} n(y)\,dy}\right)\right\}\end{aligned} \tag{5.15}$$

with

$$\hat{K}(x-a) - K(x) = \frac{n(x) - n(x-a)}{1 - \int_{x-a}^{x} n(y)\,dy}$$

Further $\Xi(x) = (1+\gamma D)\Lambda(x) = [1 + \gamma\Lambda'(x)/\Lambda(x)]\Lambda(x)$ and $\hat{\Xi}(x) = (1-\gamma D)\hat{\Lambda}(x) = [1 - \gamma\hat{\Lambda}'(x)/\hat{\Lambda}(x)]\hat{\Lambda}(x)$, so that

$$\begin{aligned} \Xi(x) &= [1 + \gamma K(x)]\Lambda(x) \\ \hat{\Xi}(x) &= [1 + \gamma\hat{K}(x)]\hat{\Lambda}(x) \end{aligned} \tag{5.16}$$

To complete the description of the sticky-core model, it follows from either (5.14) or (5.15) that

$$\Xi_T = \exp\int_{-\infty}^{\infty} \frac{1}{2\gamma}\left\{\left[1 + 2\gamma\frac{n(x+a/2) + n(x-a/2)}{1 - \int_{n-a/2}^{n+a/2} n(y)\,dy} + \gamma^2\left(\frac{n(x+a/2) - n(x-a/2)}{1 - \int_{n-a/2}^{n+a/2} n(y)\,dy}\right)^2\right]^{1/2} - 1\right\}dx \tag{5.17}$$

and then from (3.8) that

$$\beta(\mu - u(z)) = \ln n(z) - \ln[1 + \gamma K(z)] - \ln[1 + \hat{K}(z)] + \int_{-\infty}^{z} [\hat{K}(x) - K(x)]\,dx \tag{5.18}$$

Making use of

$$\begin{aligned} \frac{1}{1+\gamma K(x)} &= \frac{\hat{K}(x-a)}{n(x)}\left[1 - \int_{x-a}^{x} n(y)\,dy\right] \\ \frac{1}{1+\gamma\hat{K}(x)} &= \frac{K(x+a)}{n(x)}\left[1 - \int_{x}^{x+a} n(y)\,dy\right] \end{aligned} \tag{5.19}$$

(5.18) may be rewritten as

$$\begin{aligned} \beta(\mu - u(z)) = {} & \ln[K(z+a)\hat{K}(z-a)/n(z)] \\ & + \frac{1}{2}\ln\left(1 - \int_{z-a}^{z} n(y)\,dy\right)\left(1 - \int_{z}^{z+a} n(y)\,dy\right) \\ & + \frac{1}{2\gamma}\int_{z-a}^{z}\left\{\left[1 + 2\gamma\frac{n(x+a) + n(x)}{1 - \int_{x}^{x+a} n(y)} + \gamma^2\left(\frac{n(x+a) - n(x)}{1 - \int_{x}^{x+a} n(y)\,dy}\right)^2\right]^{1/2} - 1\right\}dx \end{aligned} \tag{5.20}$$

6. DISCUSSION

One of the primary purposes of the study of one-dimensional fluids is that of checking assumptions on the structure of fluids in which dimensionality does not seem a crucial issue. In particular, hypothetical properties of the direct correlation function $c(r_1, r_2)$ play an important role in a number of approximation methods that have been used: in PY,[8], MSM,[9] for instance, c has the range of the interaction potential. Now $c(r_1, r_2)$ is obtainable at once from the profile equation via

$$\frac{\delta(r_1 - r_2)}{n(r_1)} - c(r_1, r_2) = \frac{\delta\beta(\mu - u(r_1))}{\delta n(r_2)} \tag{6.1}$$

For example, for pure hard cores of diameter a, according to (4.9),

$$\begin{aligned} c(x_1, x_2) = &- \frac{e_0(x_1 + a - x_2) - e_0(x_1 - x_2)}{1 - \int_{x_1}^{x_1+a} n(y)\,dy} \\ &- \frac{e_0(x_1 - x_2) - e_0(x_1 - a - x_2)}{1 - \int_{x_2}^{x_2+a} n(y)\,dy} \\ &- \int \frac{\begin{gathered}[e_0(x_1 - x_2) - e_0(x_1 - a - x_3)] \\ \times [e_0(x_3 + a - x_2) - e_0(x_3 - x_2)]\end{gathered}}{\left[1 - \int_{x_3}^{x_3+a} n(y)\,dy\right]^2} n(x_3)\,dx_3 \end{aligned} \tag{6.2}$$

Thus, $c(x_1, x_2) = 0$ unless $|x_1 - x_2| \leqslant a$, in agreement with the above and in fact expressing their full content:

$$c(x_1, x_2) = 0 \qquad \text{for} \quad |x_1 - x_2| > a,$$
$$g(x_1, x_2) = 0 \qquad \text{for} \quad |x_1 - x_2| \leqslant a$$

uniquely determine g and c as functionals of the density $n(x)$. (g is the two-point radial distribution.)

For sticky hard cores, (5.20), the expression for $c(x_1, x_2)$ is a good deal more complicated. However, since $u(z)$ depends upon $n(y)$ only in the range $z - a \leqslant y \leqslant z + a$, it is still true that $c(x_1, x_2)$ vanishes beyond the range of the core, $g(x_1, x_2)$ within the range of the core. But g and c both have δ-function singularities at $|x_1 - x_2| = a$, and these must be related to complete the determination of the structure. What is now no longer true is the validity of any of the usual closures, or auxiliary relations between g and c. To see this, it suffices to look at a uniform sticky hard rod fluid, where the relevant computations are trivial. In general, for nearest neighbor potential $\phi(x - y)$ and Boltzmann factor $e(x) = \exp - \beta\phi(x)$, it is easily seen on working in an isobaric canonical ensemble that

$$\text{if} \quad 0 < x - y < 2a, \qquad \text{then} \quad ng(x-y) = e(x-y)e^{\beta(\mu(P) - P(x-y))} \tag{6.3}$$

where

$$e^{-\beta\mu(P)} = \int_0^\infty e(x)e^{-\beta P x}\,dx$$

and also that

$$1 - n\tilde{c}(k) = \frac{\left(1 - \exp\{-\beta[\mu(P + ik/\beta) - \mu(P)]\}\right)\left(1 - \exp\{-\beta[\mu(P - ik/\beta) - \mu(P)]\}\right)}{1 - \exp\{-\beta[\mu(P + ik/\beta) - 2\mu(P) + \mu(P - ik/\beta)]\}} \tag{6.4}$$

Returning to the sticky hard rods with Boltzmann factor (5.10), the δ-function singularities are then found to be

$$\begin{aligned} g(x) &= \frac{\gamma\beta P}{1 + \gamma\beta P}\delta(x - a) + \cdots \\ c(x) &= \frac{\gamma\beta P(1 + \gamma\beta P)}{1 + 2\gamma\beta P}\delta(x - a) + \cdots \end{aligned} \tag{6.5}$$

The PY closure, for example,

$$g(x)/e(x) = c(x)/[e(x) - 1] \tag{6.6}$$

would, in the singular region, require the two coefficients of $\delta(x - a)$ in (6.5) to be the same and this is in error by a term of relative order $(\gamma\beta P)^2$ for small γ.

A second, perhaps more important, motivation for one-dimensional studies is that of suggesting effective approximations for real fluids. A convenient quantity upon which to focus is the grand canonical potential

$$\Omega = -(1/\beta)\ln \Xi \tag{6.7}$$

which serves as generating functional for all expectations. Equation (4.7), for example, has been used in this fashion. Since $n(z + a)$ in the numerator of the integrand can be replaced by $n(z)$—the difference of the integrands is an obvious derivative—we can write (4.7) as

$$\Omega = -\frac{1}{\beta}\int_{-\infty}^{\infty}\frac{1}{2}\left[n\left(z + \frac{a}{2}\right) + n\left(z - \frac{a}{2}\right)\right]\bigg/\left(1 - \int_{z-a/2}^{z+a/2} n(y)\,dy\right)dz \tag{6.8}$$

a functional of the surface and volume average densities

$$
\begin{aligned}
n_\sigma(z) &= \frac{1}{2}\left[n\left(z+\frac{a}{2}\right)+n\left(z-\frac{a}{2}\right)\right] \\
n_\tau(z) &= \frac{1}{a}\int_{z-a/2}^{z+a/2} n(y)\,dy
\end{aligned}
\tag{6.9}
$$

This suggests that the grand potential of an arbitrary nonuniform fluid be modeled as

$$
\Omega[n] = \int n_\sigma(r)\omega(n_\tau(r))\,d^3r \tag{6.10}
$$

where n_σ and n_τ are suitable linear transforms of the density, e.g.,

$$
\begin{aligned}
n_\sigma(r) &= \int \sigma(r+r')n(r')\,d^3r' \\
\int \sigma(r')\,d^3r' &= 1
\end{aligned}
\tag{6.11}
$$

and ω is the specific grand potential or Pv product for the bulk fluid.

The bulk Helmholtz free energy

$$
\begin{aligned}
F^B &= F - \int n(r)u(r)\,d^3r \\
&= \Omega + \int n(r)[\mu - u(r)]\,d^3r
\end{aligned}
\tag{6.12}
$$

is a more appropriate functional of the density. Since

$$
\begin{aligned}
\Omega &= F^B - \int n(r)[\mu - u(r)]\,d^3r \\
&= \left[1 - \int n(r)\frac{\delta}{\delta n(r)}\,d^3r\right]F^B
\end{aligned}
\tag{6.13}
$$

we can, on separating out the ideal gas contribution, also write

$$
\beta F^B[n] = \int n(r)\ln n(r)\,d^3r + \int n_\sigma(r)[\beta f(n_\tau(r)) - \ln n_\tau(r)]\,d^3r \tag{6.14}
$$

The detailed fluid structure then follows from

$$
\begin{aligned}
\mu - u(r) &= \delta F^B[n]/\delta n(r) \\
\frac{\delta(r-r')}{n(r)} - c(r,r') &= \beta\delta[\mu - u(r)]/\delta n(r')
\end{aligned}
\tag{6.15}
$$

Equation (6.14) is an outrageous extrapolation based upon minimal information. The unknowns σ and τ can, however, be determined from any two pieces of bulk information on $c(r,r')$, leading to quite reasonable results.[3] There are numerous generalizations that can be used to take advantage of additional bulk data, and these will be reported in due course.

But the sticky-rod result (5.17) serves to restrict the possibilities. It is again a functional of the average densities (6.9) relevant to the pure cores, but its form

$$\Omega = -\frac{1}{2\beta\gamma}\int_{-\infty}^{\infty}\left\{\left[1 + 4\gamma\frac{n_\sigma(x)}{1 - an_\tau(x)} + \gamma^2\left(\frac{n_\tau'(x)}{1 - an_\tau(x)}\right)^2\right]^{1/2} - 1\right\}dx \tag{6.16}$$

is substantially different: there is no obvious specific free energy attached to it, and the "gradient" $n_\tau'(x)$ also makes its appearance.

In conclusion, we have seen that it is possible to analyze nontrivial nonuniform classical one-dimensional fluids, and that such analyses can contribute usefully to the study of the properties of real three-dimensional fluids. It is the properties peculiar to higher dimensionality that are given short shrift and that presumably will have to be treated by more specialized and incisive techniques.

APPENDIX

Here we define

$$\bar{Q}_N(L) \equiv \int_{-\infty}^{L} \cdots \int \prod_{i=2}^{N} e(x_i - x_{i-1}) \prod_{i=1}^{N} W(x_i) \prod_{i=1}^{N} dx_i \tag{A.1}$$

It follows that

$$\partial\bar{Q}_N(L)/\partial L = W(L)\int e(L - L')\,\partial\bar{Q}_{N-1}(L')/\partial L'\,dL'$$

or

$$\frac{\partial\bar{Q}_N(L)}{\partial L} = W(L)\int e'(L - L')\bar{Q}_{N-1}(L')\,dL' \tag{A.2}$$

from which

$$\frac{\partial\bar{\Xi}(L)}{\partial L} = w(L)\int e'(L - L')\bar{\Xi}(L')\,dL' \tag{A.3}$$

Writing $\bar{\Xi} = \exp - \beta\bar{\Omega}$, then

$$\beta(u(x) - \mu) = \beta\bar{\Omega}(x) - \ln\bar{\Omega}'(x) + \ln\int e'(x - y)e^{-\beta\bar{\Omega}(y)}\,dy \tag{A.4}$$

We now process (A.4) by first applying $\delta/\delta\bar{\Omega}(z)$:

$$\beta\frac{\delta u(x)}{\delta\bar{\Omega}(z)} = \beta\delta(x - z) - \frac{\delta'(x - z)}{\bar{\Omega}'(x)} - \beta\frac{e'(x - z)e^{-\beta\bar{\Omega}(z)}}{\int e'(x - y)e^{-\beta\bar{\Omega}(y)}\,dy} \tag{A.5}$$

But $n(x) = \lim_{v\to\infty} \delta\bar{\Omega}(v)/\delta u(x)$. Hence multiplying (A.5) by $n(x)$ and integrating over x,

$$0 = \beta n(z) + \left[\frac{n(z)}{\bar{\Omega}'(z)}\right]' - \beta \int n(x) \frac{e'(x-z)e^{-\beta\bar{\Omega}(z)}}{\int e'(x-y)e^{-\beta\bar{\Omega}(y)}\,dy}\,dx \quad \text{(A.6)}$$

If

$$Ef(x) = \int e'(x-y)f(y)\,dy$$

(A.6) can be rewritten as

$$E^*\left\{\frac{n(z)}{Ee^{-\beta\bar{\Omega}(z)}}\right\} = -\left\{\frac{n(z)}{\left[e^{-\beta\bar{\Omega}(z)}\right]'}\right\} \quad \text{(A.7)}$$

which, with the identification $\Xi = E\bar{\Xi}$, $E = e\partial/\partial x$, is equivalent to the first of (3.4).

REFERENCES

1. R. Evans, *Mol. Phys.* **42**:1169 (1981).
2. J. K. Percus, *J. Stat. Phys.* **15**:505 (1976).
3. J. K. Percus, *J. Chem. Phys.* **75**:1316 (1981).
4. J. K. Percus, in *Studies in Statistical Mechanics*, E. W. Montroll and J. L. Lebowitz, eds. (North-Holland, Amsterdam, 1982).
5. See, e.g., E. L. Ince, *Ordinary Differential Equations*, (Longmans, Green, London, 1926).
6. R. J. Baxter, *J. Chem. Phys.* **49**:2770 (1968).
7. J. K. Percus and C. J. Yevick, *Phys. Rev.* **110**:1 (1958).
8. J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **144**:251 (1966).