Journal of Statistical Physics, Vol. 15, No. 5, 1976

Model for Density Variation at a Fluid Surface[1]

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Received April 29, 1976

A fluid model with freely propagating longitudinal density waves is modified by the imposition of an external field. A relation between the resulting density inhomogeneity and the applied potential is obtained, depending only upon the uniform fluid pair distribution function. This is solved for a container-bounded fluid. The resulting surface density profiles for classical and zero-temperature Bose hard-sphere fluids compare very well with numerical experiments.

KEY WORDS: Fluid ; nonuniform ; surface ; density profile.

1. INTRODUCTION

Recent numerical work[1,2] has shed new light on the fine structure of the surface of an equilibrium fluid, be it container-limited or at a two-phase interface. Several related approximations[3-5] to the ground state of a nonuniform Bose fluid strongly suggest a decaying spatial oscillation of equilibrium density as one penetrates a fluid bounded by a wall. This has been verified by accurate Monte Carlo calculations.[2] At the other temperature extreme, the most naive layering picture for a classical hard-core fluid suggests density oscillations normal to a wall-bounded surface, which also accords with Monte Carlo results.[2] Although the Bose fluid behavior seems to lean heavily on the quantum nature of the fluid, the classical fluid behavior belies this impression. Thus the phenomenon appears more universal and perhaps directly related to other observable properties of the fluid, such as the oscillation of the radial distribution function, which it certainly resembles.

During the course of a reexamination of the somewhat dated treatment

Supported in part by U.S. ERDA, Contract No. E(11-1)-3077.

[1] Based on a talk given at Johns Hopkins Physics Colloquium, November 1974.

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alluded to above,[(3)] the writer was driven to conclude that while a practical sequential approximation procedure for nonuniform fluids remains to be found, the empirical relations implied by a very simple model (see, e.g., Ref. 6) contain the major substance of more detailed analyses. The model is characterized by the free propagation of bulk medium longitudinal density waves, and static inhomogeneities are built up from forced static amplitudes of these waves in response to an external potential. In this paper, we compare the consequences of the model for Bose and classical hard-core fluids with results of numerical experiments. The comparison indicates that this model can be regarded as a very effective zeroth-order approximation.

2. THE MODEL

We start with a uniform fluid in thermal equilibrium. The model properties to be assumed are contained in the nominally weak assumption that longitudinal density waves propagate freely in this medium:

$$d^2\hat{\rho}_k/dt^2 + \omega_k{}^2\hat{\rho}_k = 0$$

where

$$\hat{\rho}_k \equiv \int \hat{\rho}(x)e^{ik\cdot x}\, d^3x = \sum_{i=1}^{N} e^{ik\cdot x_i} \tag{1}$$

The particle number N will be regarded as sensibly infinite; it will play no role, but the uniform density n is the primary parameter to be controlled. It is not hard to push this model into internal contradictions, but it is also not hard to avoid them.

If an external potential $U = \sum U(x_i)$ is now applied, then with the tacit assumption of velocity-independent internal forces so that $\dot{x}_i = p_i/m$, the change in the Hamiltonian $\Delta H = U$ will change the equations of motion by

$$\begin{aligned}
&(i/\hbar)[\Delta H, d\hat{\rho}_k/dt] \\
&\quad = (i/\hbar)\left[\sum U(x_i), \sum (ik\cdot p_i/2m)e^{ik\cdot x_i} + \sum e^{ik\cdot x_i} ik\cdot p_i/2m\right] \\
&\quad = (-i/m)\sum k\cdot\nabla U(x_i)e^{ik\cdot x_i} \\
&\quad = -(1/m)\sum \nabla U(x_i)\cdot\nabla e^{ik\cdot x_i} = -(1/m)\int \hat{\rho}(x)\nabla U(x)\cdot\nabla e^{ik\cdot x}\, d^3x \\
&\quad = (1/m)\int e^{ik\cdot x}\nabla\cdot[\hat{\rho}(x)\nabla U(x)]\, d^3x
\end{aligned}$$

It is convenient to introduce the operator $\hat{W}(x)$ as one which satisfies[3]

$$n\nabla^2\hat{W}(x) = \nabla\cdot[\hat{\rho}(x)\nabla U(x)] \tag{2}$$

[3] See also Ref. 3, p. II-233, and Ref. 6.

essentially weighting the force field by the local density. The equations of motion then become

$$d^2\hat{\rho}_k/dt^2 + \omega_k{}^2\hat{\rho}_k = -(n/m)k^2\hat{W}_k \tag{3}$$

with the subscript k generally denoting Fourier transform. Now Eq. (3) is of course that of a forced harmonic oscillator. Since $\langle d^2\hat{\rho}_k/dt^2\rangle = 0$, we have on taking mean values

$$\rho_k = -(nk^2/m\omega_k{}^2)W_k, \qquad n\nabla^2 W(x) = \nabla\cdot[\rho(x)\nabla U(x)] \tag{4}$$

where $\rho_k = \langle\hat{\rho}_k\rangle$, $W_k = \langle\hat{W}_k\rangle$, and $k \neq 0$.

In order to apply (4), we must eliminate the model frequencies ω_k in favor of direct fluid parameters. For this purpose, let us look at the uniform system structure factor

$$S(k) = 1 + nh_k = (1/N)\langle\rho_k\hat{\rho}_{-k}\rangle \tag{5}$$

where $g = h + 1$ is the radial distribution function. The quantity $\langle\rho_k\hat{\rho}_{-k}\rangle = \mathrm{Tr}\,\frac{1}{2}(\hat{\rho}_k\hat{\rho}_{-k} + \hat{\rho}_{-k}\rho_k)e^{-\beta H}/(\mathrm{Tr}\,e^{-\beta H})$ is readily obtained from the equations of motion if the ω_k are really c-numbers. Since (1) is solved as

$$\hat{\rho}_k(t) = [\cos(\omega_k t)]\hat{\rho}_k(0) + \frac{1}{\omega_k}[\sin(\omega_k t)]\, d\hat{\rho}_k(0)/dt \tag{6}$$

it follows that $e^{\beta H}\hat{\rho}_k e^{-\beta H} = [\cosh(\beta\hbar\omega_k)]\hat{\rho}_k - (i/\omega_k)[\sinh(\beta\hbar\omega_k)]\, d\hat{\rho}_k/dt$ and hence that

$$\mathrm{Tr}(\hat{\rho}_{-k}\hat{\rho}_k e^{-\beta H}) = \frac{i}{\omega_k}\frac{\sinh(\beta\hbar\omega_k)}{\cosh(\beta\hbar\omega_k) - 1}\,\mathrm{Tr}\left(\rho_{-k}\frac{d\hat{\rho}_k}{dt}e^{-\beta H}\right) \tag{7}$$

The addition of $\mathrm{Tr}(\hat{\rho}_k\hat{\rho}_{-k}e^{-\beta H})$ brings in the commutator $[\hat{\rho}_{-k}, d\hat{\rho}_k/dt]$ and on evaluation we find

$$S(k) = (\hbar k^2/2m\omega_k)\coth(\tfrac{1}{2}\beta\hbar\omega_k) \tag{8}$$

The ω_k are most expeditiously eliminated from (4) and (8) at low and high (classical) temperature, yielding the key model expressions

$$\rho_k = \begin{cases} -4(mn/\hbar^2k^2)S(k)^2 W_k, & T\to 0 \\ -n\beta S(k)W_k, & T\to\infty \end{cases} \tag{9}$$

3. CLASSICAL DOMAIN

Let us in this section focus on the high-temperature or classical regime. It will be useful to make contact with two familiar limiting situations. In the first case, (4) and (9) are preferably written in terms of the direct correlation function, which for our purposes may be defined by[4]

$$S(k) = 1/(1 - nc_k) \tag{10}$$

[4] For a review of the concepts associated with classical Ornstein–Zernike theory in modern guise, see Ref. 7.

Reverse Fourier-transforming, we then have from (4) and (9)

$$\rho(x) + n\int c(x-y)\rho(y)\,d^3y + (\nabla^2)^{-1}\nabla\cdot[\rho(x)\,\nabla\beta U(x)] = \text{const} \quad (11)$$

which has also appeared in a different context (Ref. 7, p. II-65). Now, let us suppose that, due to similar behavior of $U(x)$, $\rho(x)$ is a slowly varying function on the scale of the range of $c(x)$. Hence

$$\rho(x) + n\int c(x-y)\rho(y)\,d^3y \sim \left[1 + n\int c(y)\,d^3y\right]\rho(x)$$
$$= \rho(x)\,\partial\beta P/\partial n$$

where $P(n)$ is the system pressure, and (11) may be rewritten as

$$\nabla\cdot[(\partial P/\partial n)\,\nabla\rho(x) + \rho(x)\,\nabla U(x)] = 0 \quad (12)$$

Equation (12) will be recognized as a consequence of the Archimedean or local thermodynamic balance of forces $\nabla P(\rho) + \rho\,\nabla U = 0$ in any region in which $\partial P/\partial\rho$ can be regarded as constant.

In the second extreme, we imagine $U(x)$ small enough to be regarded as a perturbation $\delta U(x)$. Then $\rho(x) = n + \delta\rho(x)$ and $W(x) = \delta U(x)$ to leading order. Hence (9) transformed back to coordinate space reads

$$\delta\rho(x) = \int -\beta\,\delta U(y)[n^2 g(x-y) - n^2 + n\,\delta(x-y)]\,d^3y \quad (13)$$

which is known to be the exact linear response[7] of the local density to an external perturbation (an additive constant not appearing if the chemical potential is fixed).

It is also interesting to consider a uniform mixture of fluid particles and of vanishing density fictitious wall particles, each of which exerts a wall potential. The joint correlation function $h_w(x, 0)$ for a fluid particle at x and a wall particle at the origin becomes precisely $\rho(x)/n - 1$, and the Ornstein–Zernike definition of the joint direct correlation function $c_w(x) \equiv c_w(x, 0)$ reads[7]

$$\rho(x)/n - 1 = c_w(x) + n\int h(x-y)c_w(y)\,d^3y \quad (14)$$

This is simply the nonperturbative version of (13), with the identification $-\beta W(x) = c_w(x)$. Of course, the "wall" particle can exert any desired field as well.

In the problem of immediate interest, the external potential is that of a (planar) wall defined by

$$U(x) = \begin{cases} \infty, & x_1 < 0 \\ 0, & x_1 > 0 \end{cases} \quad (15)$$

How do we deal with this? To start with, reliable bulk data in the form of $S(k)$ are required. Since $S(k)$ is known exactly for one-dimensional hard cores, and quite well via the PY approximation[8] for three-dimensional hard cores, these are the cases we will emphasize. There are then three approaches available, all ultimately equivalent. In the first, we observe that since $\rho(x) = 0$ when $U(x) = \infty$, the product $\rho\ \nabla U$ entering into W is indeterminate when $x_1 < 0$, but certainly vanishes when $x_1 > 0$ since $U = 0$, with ρ finite in this region. $W(x)$ may clearly be chosen to have the same properties, and so we have

$$\begin{gathered} \rho_k = -n\beta S(k) W_k, \qquad k \neq 0 \\ \rho(x) = 0 \quad \text{for} \quad x_1 < 0; \qquad \rho(x) \to n \quad \text{for} \quad x_1 \to \infty \\ W(x) = 0 \qquad \text{for} \quad x_1 > 0 \end{gathered} \tag{16}$$

Equations (16) are indeed sufficient to determine the density $\rho(x)$.

A second approach involves using the valid linear response relaxation (13) out of its perturbative region of validity. Since a hard-wall potential is to be inserted, one has available the hard-core insertion[9] or mean spherical model[10] approximation in which the actual potential in an approximate theory is replaced by an effective potential, vanishing outside the "core," determined by the condition that the density vanish inside the core. Thus (16) is exactly reproduced, with W as the effective potential.

Finally, if h in (14) is taken for hard cores in PY approximation and $c_w = -\beta W$ satisfies (16), one is simply saying that all direct correlations vanish outside infinite potential regions, all densities inside. Since a planar wall is the large-radius limit of a hard sphere, (14) then represents a PY hard-sphere mixture, which has been solved,[11] in which one component has infinite radius but zero density and is adjusted to cover the negative x_1 half-space. This limit is readily taken.

4. HARD-CORE FLUID AT WALL

For a fluid at a wall, we must solve Eqs. (16). This may be done in principle by a standard Wiener–Hopf technique (see, e.g., Ref. 12). We first observe that $\rho(x)$ and $W(x)$ will be uniform except in the x_1 direction, so that $k_2 = k_3 = 0$ throughout, and x, k will hereafter refer to one-dimensional variables. The solution of (16) then depends upon the properties of the functions involved in the complex k plane. Except at a singular thermodynamic state, $\rho'(x)$ will be absolutely integrable, and it follows that $-ik\rho_k = \int_0^\infty \rho'(x)e^{ikx}\,dx$ is analytic and bounded for $\operatorname{Im} k \geqslant 0$. Conversely, $-ikW_k = \int_{-\infty}^0 W'(x)e^{ikx}\,dx$ is expected to be analytic and bounded for $\operatorname{Im} k \leqslant 0$.

$S(k)$, obtained experimentally from X-ray or neutron scattering, is not initially defined for complex k. For real k, we have first $S(k) = 1 + nh_k \to 1$ as $|k| \to \infty$, since $h(x)$ is not singular. Further, $S(k) = (1/N)\langle|\hat{\rho}_k|^2\rangle > 0$ and bounded for real k for nonsingular states. Consequently, $S(k)$ can be extended to the complex plane and may be represented by the Wiener–Hopf factorization

$$S(k) = S_+(k)/S_-(k) \tag{17}$$

where $S_+(k)$ is analytic, bounded above and below (away from 0) in the half-plane $\operatorname{Im} k \geqslant c_-$, a negative number, while $S_-(k)$ has the same properties for $\operatorname{Im} k \leqslant c_+$, a positive number. Indeed, one has explicit formulas for $S_\pm(k)$, which for real k reduce to

$$S_\pm(k) = S(k)^{\pm 1/2}\left[\exp(1/2\pi i)P\int_{-\infty}^{\infty} \ln S(q)\, dq/(q-k)\right] \tag{18}$$

where P denotes principal part. Now from (16) and (17)

$$-ik\rho_k/S_+(k) = -n\beta(-ikW_k)/S_-(k) \tag{19}$$

Since the left-hand side is analytic and bounded for $\operatorname{Im} k \geqslant 0$, the right-hand side for $\operatorname{Im} k \leqslant 0$, the common function must be a constant: $-ik\rho_k = cS_+(k)$. To evaluate the constant, we note that

$$\lim_{k\to 0} -ik\rho_k = \int_{-\varepsilon}^{\infty} \rho'(x)\, dx = \rho(x)\Big|_{-\varepsilon}^{\infty} = n$$

Hence $c = n/S_+(0)$, and

$$\rho_k = \frac{in}{k}\frac{S_+(k)}{S_+(0)}, \qquad W_k = -\frac{i}{\beta k}\frac{S_-(k)}{S_-(0)}, \qquad \text{for} \quad k \neq 0 \tag{20}$$

the desired solution. If the explicit (18) is used, then since $S(q)$ is an even function, we have as well $S_\pm(0) = S(0)^{1/2}$.

The function $S(k)$ is known exactly (see, e.g., Ref. 13) for a system of one-dimensional hard rods, and may be written as

$$S(k) = \frac{k}{\beta P(1 - e^{ika}) - ik}\Bigg/\frac{\beta P(1 - e^{-ika}) + ik}{k} \tag{21}$$

where a is the hard-rod diameter and P is the system pressure. Since (21) can be seen to be precisely the Wiener–Hopf factorization, we have at once [using $n = \beta P/(1 + Pa)$]

$$\rho_k = \beta P/[\beta P(1 - e^{ika}) - ik] \tag{22}$$

which is the exact known result.[5] The effective wall potential is readily

[5] See, e.g., Ref. 7, p. 136.

transformed back to coordinate space, or obtained from a mixture of one-dimensional cores via $c_w(x) = -\beta W(x)$, and (14), and we find

$$W(x) = \begin{cases} 0, & x > 0 \\ [1 - n(x + a)]\, \partial P/\partial n, & -a \leqslant x \leqslant 0 \\ \partial P/\partial n, & x \leqslant -a \end{cases} \tag{23}$$

a step function aside from a surface region of depth a.

For a three-dimensional hard-core fluid, analytic expressions are available neither for $S(k)$ nor for the density profile $\rho(x)$. However, $S(k)$ can be supplied with reliability by the PY approximation, which can be written in the form

$$\begin{aligned} S(k) &= (1 - \eta)^4 \frac{k^3}{R(-ik) + L(-ik)e^{ik}} \Big/ \frac{R(ik) + L(ik)e^{-ik}}{k^3} \\ L(t) &\equiv 12\eta[(1 + \tfrac{1}{2}\eta)t + (1 + 2\eta)] \\ R(t) &\equiv (1 - \eta)^2 t^3 + 6\eta(1 - \eta)t^2 + 18\eta^2 t - 12\eta(1 + 2\eta) \end{aligned} \tag{24}$$

where $\eta \equiv \pi n/6$ and the hard-core diameter is chosen as $a = 1$. The numerator and denominator of (24) can be shown to have no zeros in their appropriate domains,[8] so that (24) is again a Wiener–Hopf factorization. It follows on carrying out the necessary evaluation at $k = 0$ that

$$\rho_k = -(6/\pi)\eta(1 + 2\eta)k^2/[R(-ik) + L(-ik)e^{ik}] \tag{25}$$

and that

$$W(x) = \begin{cases} 0, & x > 0 \\ [1 + \frac{1}{3}\pi n(x + 1)^3]\, \partial P/\partial n, & -1 \leqslant x \leqslant 0 \\ \partial P/\partial n, & x \leqslant -1 \end{cases} \tag{26}$$

These results can also be obtained, as in the one-dimensional case, by solving the PY approximation for a mixture of two hard-core fluids and letting the core diameter of one fluid go to infinity as its density goes to zero.

Numerical Fourier analysis to extract $\rho(x)$ is readily performed. However, in comparing with Monte Carlo simulation data on $\rho(x)$, two technical problems arise. First, for obvious physical reasons, the container chosen in the simulation has two walls rather than one. However, if the $\rho(x)$ relevant to a single wall decays to its asymptotic value n within the distance L of the second wall, and similarly $W(x)$ to $W_{\rm as}$, it is easy to verify that

$$\bar{\rho}(x) = \rho(x) + \rho(L - x) - n, \qquad \bar{U}(x) = U(x) + U(L - x) - U_{\rm as} \tag{27}$$

satisfies all conditions for the box. Second, in numerical work, it is the total particle number, or mean density n_{av}, not the asymptotic density n, which is fixed. Now

$$\begin{aligned} n_{av} &= L^{-1}\int_0^L [\rho(x) + \rho(L-x) - n]\,dx \\ &= (2/L)\int_0^L [\rho(x) - n]\,dx + n \\ &= n + (2/L)\int_0^\infty [\rho(x) - n]\,dx \\ &= n + (2/L)\lim_{k\to 0}\int_0^\infty [\rho(x) - n]e^{ikx}\,dx \\ &= n + (2/L)\lim_{k\to 0}(\rho_k - in/k) \end{aligned}$$

Inserting (25), then,

$$n_{av} = n + \frac{3}{2L}\frac{n^2}{n + (3/\pi)} \tag{28}$$

[(28) is also related to the interfacial free energy, a problem which will not be considered in the present context.]

A comparison between the Monte Carlo results[2] at $n_{av} = 0.7$ and the Fourier transform of (25) shows (Fig. 1) effective identity for $x > 0.1$, with

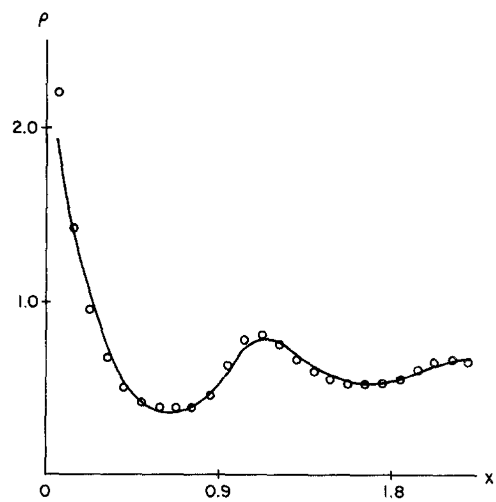

Fig. 1. Comparison of density profiles for a classical fluid of unit-diameter hard cores at a reference density $n = 0.609$ in a box of width $L = 4.5$. Monte Carlo results are indicated by the open circles, the present approximation by the solid curve.

slight deviations in the numerically less accurate, rapidly rising $x < 0.1$ regime (see also Ref. 14).

5. COMMENTS ON CLASSICAL FLUID RESULTS

The numerical tests that we have made of the basic approximation (16) have certainly been gratifying. Further, integrating out the two irrelevant dimensions in (14) for a planar wall and using the $W(x)$ notation, we have for $x > 0$

$$\rho(x) = n + 2\pi n^2\beta \int_0^\infty \left[\int_{-y}^0 W(z)\,dz\right](y + x)h(y + x)\,dy \tag{29}$$

showing the reason for the resemblance of $\rho(x)$ to the pair correlation: There are essentially two contributions, one due to the spike in $W(z)$ near the origin, yielding $\propto xh(x)$, and the other to the asymptotic value of W, with a second derivative going as $xh(x)$. The former would be produced, except for amplitude, by regarding the wall as a continuous fixed particle.

The numerical differences shown in Fig. 1 cannot, however, be lightly dismissed, for they indicate a basic deficiency in the approximation. The point is this. One knows that the infinite wall force effectively decouples the adjacent fluid, so that the ideal gas equation of state

$$\rho(0) = \beta P \tag{30}$$

holds exactly. On the other hand, the wall density is given in terms of the approximate density profile by

$$\rho(0) = \rho(x)\Big|_{0-}^{0+} = \lim_{k\to\infty} \int \rho'(x)e^{ikx}\,dx = \lim_{k\to\infty} - ik\rho_k$$

or according to (18) and (20), $\rho(0) \sim n/S(0)^{1/2}$. But from the familiar relation[7] $S(0) = \partial n/\partial\beta P$, then

$$\rho(0) \sim n(\partial\beta P/\partial n)^{1/2} \tag{31}$$

Equations (30) and (31) coincide for the hard-rod equation of state $\beta P = n/(1 - na)$, and only then. Thus, even if the exact $S(k)$ were used instead of the PY approximation [which is really the bulk fluid counterpart of (16)] to modify (25), there would be a discrepancy in the density profile at the wall. Since the discrepancy in Fig. 1 decays very rapidly, it is tempting to attribute it to a neglected surface mode. But this is only one of several pictures which may be used to improve the agreement, which we shall not discuss further at this time.

6. BOSE FLUID AT A WALL

We proceed to the quantum mechanical $T = 0°$ domain. The approximate nature of the formulation (9) is now much more evident. To start with, it is true that if isothermal longitudinal acoustic phonons are pure excitations, one will have $\lim_{k\to 0} \omega_k/k = c = (\partial P/\partial mn)^{1/2}$, so that (12) again holds for slowly varying applied field. But the interrelation (8), or $\omega_k = \hbar k^2/2mS(k)$ in the $T \to 0°$ limit, is a consequence of the basic Feynman approximation[15] and is certainly not exact, even as $k \to 0$.

Going to the opposite extreme, for weak applied field, (9) avers the linear response function $\delta\rho_k/\delta U_k = -4(mn/\hbar k^2)S(k)^2$, which is demonstrably not an exact result. For example, for one-dimensional zero-diameter Bose hard cores, equivalent in coordinate space probability to spinless free fermions, it is easy to check that

$$\frac{\delta\rho_k}{\delta U_k} = -\frac{m}{\pi\hbar^2 k}\ln\left|\frac{2n\pi + k}{2n\pi - k}\right|,$$

$$-\frac{4mn}{\hbar}\left(\frac{S(k)}{k}\right)^2 = -\frac{4mn}{\hbar}\operatorname{Min}\left(\frac{1}{(2\pi n)^2}, \frac{1}{k^2}\right) \tag{32}$$

identical for small k or large k, but only then. Admittedly, this example is also an extreme case, highly colored by a very regular nodal structure in N space and a resulting characteristic Fermi wave number $k_f = n\pi$. Indeed, our linear response function would also be a consequence of the Bogoliubov–Zubarev approach.[16]

A better test of (9) as an adequate leading approximation would be to apply it to a more realistic nonuniform quantum fluid. For a fluid bounded by a planar wall, (9) of course transcribes at once to

$$\begin{gathered}\rho_k = -(4mn/\hbar^2)[S(k)/k]^2 W_k \\ \rho(x) = 0 \quad \text{for} \quad x_1 < 0; \qquad \rho(x) \to n \quad \text{for} \quad x_1 \to \infty \\ W(x) = 0 \qquad \text{for} \quad x_1 > 0\end{gathered} \tag{33}$$

solvable once more in principle by a Wiener–Hopf factorization. $S(k)$ is only known numerically. A plot (Fig. 2) of the relevant quantity $(S/k)^2$ for a hard-core Bose fluid (obtained from Monte Carlo simulation) shows a very strong peak in the "roton" region[6] of the spectrum, quite well represented in the present case by a Lorentzian fit

$$\left(\frac{S(k)}{k}\right)^2 = \frac{\mathrm{A}}{(k - k_1)^2 + k_2^2} + \frac{\mathrm{A}}{(k + k_1)^2 + k_2^2} \tag{34}$$

[6] See also discussion in Ref. 4.

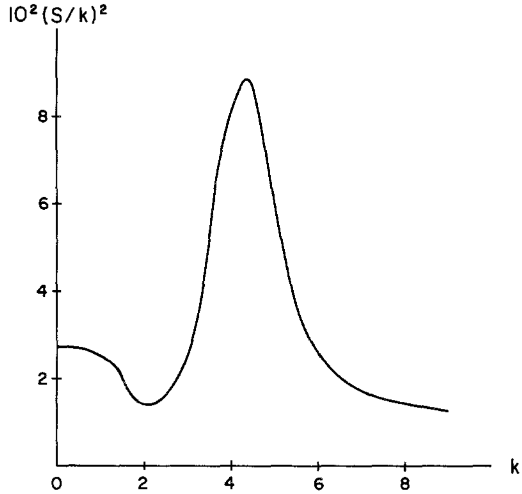

Fig. 2. $[S(k)/k]^2$ for a uniform Bose fluid of unit-diameter hard cores at a density $n = 0.204$.

Now a Wiener–Hopf factorization is trivial. ρ_k is simply the rational fractional part of (34) without poles or zeros in the upper half-plane, and with normalization via $\rho_k \to in/k$ as $k \to 0$. We find

$$\rho_k = -n(k_1^2 + k_2^2)^{1/2} \frac{k + i(k_1^2 + k_2^2)^{1/2}}{k(k - k_1 + ik_2)(k + k_1 + ik_2)} \tag{35}$$

or, on Fourier-transforming,

$$\rho(x) = n\left(1 - \frac{\cos(k_1 x + \frac{1}{2}\phi)}{\cos \frac{1}{2}\phi} e^{-k_2 x}\right) \tag{36}$$

where $\tan \phi = k_1/k_2$.

In the Monte Carlo simulation[(2)] of a Bose fluid at a wall, one has data on $n_{\text{av}} = 0.2$ in core units. At $n = 0.204$, a best fit for $S(k)$[(19),7] yields $k_1 \sim 4.2$, $k_2 \sim 0.91$. The "experimental" values are seen (Fig. 3) to be matched to within experimental error by the expression (36). Here the corrections corresponding to (27) and (28) have again been made, yielding[8] the above asymptotic $n = 0.204$, and the wall has again been defined by $\rho(x) = 0$ for $x \leqslant 0$. Once more, it should be pointed out that the apparently excellent agreement does not stand up under very detailed analysis, in particular right next to the wall. Since the wave function vanishes linearly in each variable at the wall, the density must vanish quadratically, contrary to (36).

[7] The density extrapolation has been made via Ref. 3, p. 316.

[8] In the readily derivable form $n_{\text{av}}/n = 1 - (\sin \frac{1}{2}\phi)/L(k_1^2 + k_2^2)^{1/2}$.

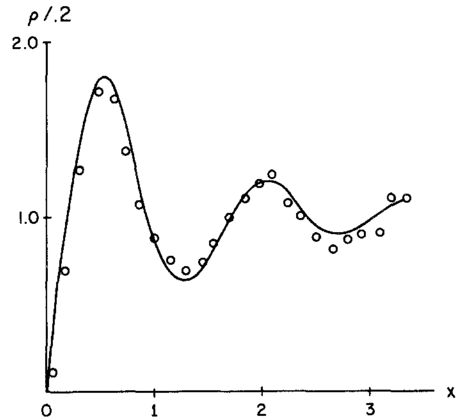

Fig. 3. Comparison of density profiles for a Bose fluid of unit-diameter hard cores at a mean density $n_{av} = 0.2$ and a temperature $T = 0°$ in bow of width $L = 6.8$. Notation as in Fig. 1.

While the qualitative difference may be attributed to the smoothing of the high-k hard-core oscillations in the representation (34), one can also make a quantitative assessment, which is unlikely to be met. For a wall of constant height $V \to \infty$ for $x < 0$, any particle coordinate $x < 0$ will be decoupled from the others, yielding a wave function $\psi = A \exp[(2mV/\hbar^2)^{1/2}x]$ for $x < 0$, or $\psi = A[1 + (2mV/\hbar^2)^{1/2}x]$ for small $x > 0$. The wall force is $P = \langle V\,\delta(x)\rangle = VA^2$, and so the local density for $x > 0$ becomes the quadratic $\rho(x) = \lim_{V\to\infty} \psi(x)^2 = (2mP/\hbar^2)x^2$. One consequence is the quantum mechanical wall equation of state

$$P = \frac{\hbar^2}{4m} \frac{\partial^2}{\partial x^2} \rho(x) \bigg|_{x=0} \tag{37}$$

replacing the classical (30).

We conclude that for quantum as well as classical fluids, a number of aspects of nonuniform systems may be obtained with surprising accuracy from readily available bulk data. It is easy enough to point out the inadequacies of the approximation method we have investigated, but less easy to formulate a systematic correction procedure based upon it.

ACKNOWLEDGMENTS

I would like to thank Drs. M. H. Kalos and K. S. Liu for numerous valuable discussions, and the staff of the Courant Institute ERDA Mathematics Computing Laboratory CDC 6600 computer for their help in the numerical work required for this paper.

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