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Shielded Distribution Approximation for a Wall-Bounded Classical Fluid

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We investigate lower order distribution functions in classical fluids in the presence of large-scale inhomogeneities, in particular those imposed by wall contacts. The consequences of the effective shielding of a wall by the nearest particle of the set being considered are determined in the context of two distribution function hierarchies, kinematic and dynamic in origin. The effects of both flat and spherical, hard and soft walls are considered, as well as those of curved and double walls. A few correction sequences to the basic shielding approximation are discussed.

KEY WORDS: Classical fluids; large-scale inhomogeneities; wall contacts; distribution functions; shielded distribution approximation.

1. INTRODUCTION

The study of inhomogeneous fluids has expanded greatly in recent years. On the one hand, classical thermodynamic arguments applied to weak inhomogeneities have been rigorously verified (see, e.g., Ref. 1). On the other hand, strong inhomogeneities, ranging from two-phase interfaces[2–6] to hard-wall boundaries,[7–11] have been the subject of extensive numerical and analytical investigation (see Refs. 12 and 13 for recent reviews). It is the topic of externally imposed boundaries that we intend to pursue in this paper.

In sequence, we first introduce the concept of shielding of distributions and the accompanying approximation hierarchy. We then recall the two major distribution function hierarchies, based respectively on direct correlation functions and upon Ursell correlations. We indicate the peculiar advantages of the latter for the present approximation scheme, and apply it to a

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hard-sphere fluid bounded by a hard wall. Generalization to softened interaction potentials then follows, as well as to softened and nonflat walls. Extension is also made to containment by more than one wall. A few illustrative examples are presented. Finally, a systematic correction sequence is set up and discussed in a preliminary way.

2. SHIELDING OF DISTRIBUTIONS

It is a truism in classical equilibrium statistical mechanics that a little dynamics goes a long way. What this means is that whereas a system can be described either realistically by a time average, or much more conveniently in computation by a phase space average, an intermediate strategy is often superior: one selects a few mode variables to follow in time and supplies the remaining variables via a phase space average. Although this division is not often used explicitly, its implicit use is widespread. An example that is particularly relevant to the present discussion occurs in the analysis of low-pressure two-phase liquid–gas interfaces. It has been found[4] that two-particle correlations normal to the interface are very well represented by imagining that the density profile is the average of the motions of a sharp interface which retains its integrity long enough for bulk equilibrium to be established in its reference frame. Thus if z is the direction normal to the interface, and ξ the normal or longitudinal location of the interface, the short time system density for liquid on the right and nominally zero-density gas on the left is represented by

$$n_\xi(z) = n_0 \epsilon(z - \xi) \tag{2.1}$$

Here ϵ is the unit step function and n_0 the bulk liquid density.

Now if, at a given transverse location $\mathbf{x} = (x, y)$, ξ is distributed according to the probability $f(\xi)$, we have the equilibrium average

$$n(z) = n_0 \int \epsilon(z - \xi) f(\xi)\, d\xi = n_0 \int_{-\infty}^{z} f(\xi)\, d\xi \tag{2.2}$$

It further follows from the corresponding Ansatz for the pair distribution

$$n_{2\xi}(\mathbf{r}, \mathbf{r}') = n_0^2 g(\mathbf{r} - \mathbf{r}') \epsilon(z - \xi) \epsilon(z' - \xi) \tag{2.3}$$

with g the bulk fluid radial distribution, that

$$\begin{aligned} n_2(\mathbf{r}, \mathbf{r}') &= n_0^2 \int g(\mathbf{r} - \mathbf{r}') \epsilon(z - \xi) \epsilon(z' - \xi) f(\xi)\, d\xi \\ &= n_0^2 g(\mathbf{r} - \mathbf{r}') \int_{-\infty}^{\min(z,z')} f(\xi)\, d\xi = n_0 n(z_{\min}) g(\mathbf{r} - \mathbf{r}') \end{aligned} \tag{2.4}$$

It is (2.4) that has been verified to surprising accuracy when $\mathbf{r}$ and $\mathbf{r}'$ have the same transverse location so that the transverse structure of the interface is irrelevant. In precisely the same fashion, we can derive the approximation

$$n_s(\mathbf{r}_1,..., \mathbf{r}_s) = n_0^{s-1} n(z_{\min}) g_s(\mathbf{r}_1,..., \mathbf{r}_s) \tag{2.5}$$

with g_s the dimensionless s-body bulk distribution function.

The expression (2.2) clearly requires that $n(z)$ increase monotonically with z. If this is not the case, as in the oscillating profile of a wall-bounded fluid, the above physical justification for (2.4) is lost. It can be recovered[14] by adopting a more complicated "intrinsic profile" than that given by (2.1), but this becomes considerably more ad hoc. The relation (2.4), however, has a far greater range of validity. To see this, one need only look at the case of a wall-bounded, one-dimensional, hard-core fluid. The distribution functions of the bulk fluid are known to be given[15] by the ordered superposition principle

$$n_s(z_1, z_2,..., z_s) = n_0{}^s g(z_1 - z_2) g(z_2 - z_3) \cdots g(z_{s-1} - z_s) \tag{2.6}$$

for $z_1 \leqslant z_2 \cdots \leqslant z_s$, where g is again the bulk radial distribution. If the cores are of diameter a, insertion of a single wall w restricting the particle centers to $z \geqslant 0$ is equivalent to placing a particle at $z = -a$:

$$n_s(z_1,..., z_s|w) = n_{s+1}(-a, z_1,..., z_s)/n_0 \tag{2.7}$$

In particular, from (2.9),

$$n(z|w) = n_0 g(z + a) \tag{2.8}$$

and it follows that (2.7) may be rewritten as

$$n_s(z_1,..., z_s|w) = n(z_{\min}|w) n_s(z_1,..., z_s)/n_0 \tag{2.9}$$

Thus the relation (2.5) holds exactly.

The justification for (2.4) is intuitively obvious in the one-dimensional hard-core system: if $-a < z_1 < z_2$, the fixing of particle 1 renders the distribution to the right of 1 independent of the conditions on its left. Thus

$$n(z_2|z_1, w) = n(z_2|z_1) \tag{2.10}$$

or

$$n(z_2, z_1|w)/n(z_1|w) = n_2(z_2, z_1)/n_0 \tag{2.11}$$

Hence

$$n_2(z_2, z_1|w) = n(z_1|w) n_2(z_2 - z_1)/n_0 \tag{2.12}$$

identical with (2.4). Summing up, (2.4) is a consequence of the fact that $z_{\min}$ shields the particles to the right from the influence of the wall to the left, and this generalizes at once to (2.9).

To what extent is the shielding argument extendable to three-dimensional space? This depends upon the extent to which the particles in question are shielded from external control by their neighbors. Suppose, for example, that we have a single wall described by $z \leqslant 0$, and that $\mathbf{r}_s$ is the furthest from the wall of s identified particles *with hard cores* (Fig. 1),

$$z_s \geqslant z_i, \qquad i = 1,\ldots, s-1 \tag{2.13}$$

all of which are constrained transversely:

$$|\mathbf{x}_i - \mathbf{x}_j| < b, \qquad i, j = 1,\ldots, s \tag{2.14}$$

where $\mathbf{x} \equiv (x, y)$. It is clear then that for large s, $n(\mathbf{r}_s)$ will be independent of the presence of the wall:

$$n(\mathbf{r}_s|\mathbf{r}_1,\ldots, \mathbf{r}_{s-1}, w) = n(\mathbf{r}_s|\mathbf{r}_1,\ldots, \mathbf{r}_{s-1}) \tag{2.15}$$

(and, for that matter, of the particles close to the wall). Equation (2.15) can be written as

$$n_s(\mathbf{r}_1,\ldots, \mathbf{r}_s|w)/n_{s-1}(\mathbf{r}_1,\ldots, \mathbf{r}_{s-1}|w) = n_s(\mathbf{r}_1,\ldots, \mathbf{r}_s)/n_{s-1}(\mathbf{r}_1,\ldots, \mathbf{r}_{s-1})$$

and hence in general as

$$n_s(r_1,\ldots, r_s|w) = n_s(r_1,\ldots, r_s)\,\frac{n_{s-1}(\mathbf{r}_1,\ldots, \hat{\mathbf{r}}_{\max},\ldots, \mathbf{r}_s|w)}{n_{s-1}(\mathbf{r}_1,\ldots, \hat{\mathbf{r}}_{\max},\ldots, \mathbf{r}_s)} \tag{2.16}$$

where $\hat{\mathbf{r}}_{\max}$ indicates the absence of the particle of maximum z. On the other hand, the strongest statement emanating from the shielding idea would be that $\mathbf{r}_1$ shields $\mathbf{r}_2,\ldots, \mathbf{r}_s$ from the wall, yielding now

$$n_{s-1}(\mathbf{r}_2,\ldots, \mathbf{r}_s|w\mathbf{r}_1) = n_{s-1}(\mathbf{r}_2,\ldots, \mathbf{r}_s|\mathbf{r}_1)$$

Thus

$$n_s(\mathbf{r}_1,\ldots, \mathbf{r}_s|w)/n(\mathbf{r}_1|w) = n_s(\mathbf{r}_1,\ldots, \mathbf{r}_s)/n(\mathbf{r}_1)$$

so that

$$n_s(\mathbf{r}_1,\ldots, \mathbf{r}_s|w) = \frac{n(\mathbf{r}_{\min}|w)}{n_0}\, n_s(\mathbf{r}_1,\ldots, \mathbf{r}_s) \tag{2.17}$$

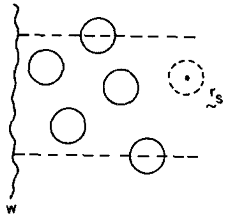

Fig. 1. Shielding configuration.

We may refer to (2.16) and (2.17) as the extreme cases $t = s - 1$ and $t = 1$, respectively, of the t-body shielding approximation for the s-body distribution.

As we have observed, the wall w in (2.15) need not be a physical wall. It can refer to another particle at $z = 0$. Then

$$n_s(\mathbf{r}_2, \ldots, \mathbf{r}_{s+1} | \mathbf{r}_1) = n_{s+1}(\mathbf{r}_1, \ldots, \mathbf{r}_{s+1})/n(\mathbf{r}_1)$$

and (2.16) becomes

$$n_{s+1}(\mathbf{r}_1, \ldots, \mathbf{r}_{s+1}) = n_s(\mathbf{r}_1, \ldots, \hat{\mathbf{r}}_{\min}, \ldots, r_{s+1}) \times \frac{n_s(\mathbf{r}_1, \ldots, \hat{\mathbf{r}}_{\max}, \ldots, \mathbf{r}_{s+1})}{n_{s-1}(\mathbf{r}_1, \ldots, \hat{\mathbf{r}}_{\min}, \hat{\mathbf{r}}_{\max}, \ldots, \mathbf{r}_{s+1})} \tag{2.18}$$

a shielded distribution superposition principle. For example, taking $s = 2$, with particle positions $\mathbf{r}_<$, $\mathbf{r}_M$, and $\mathbf{r}_>$, we have from either (2.16) or (2.17)

$$n_3(\mathbf{r}_<, \mathbf{r}_M, \mathbf{r}_>) = n_2(\mathbf{r}_M, \mathbf{r}_>) n_2(\mathbf{r}_<, \mathbf{r}_M)/n(\mathbf{r}_M) \tag{2.19}$$

obviously mimicking the situation for one-dimensional cores. In reality, (2.18) will be valid only for large s, but for any ordering direction with respect to which the transverse extension of the set of identified particles is restricted.

3. KINEMATIC HIERARCHIES

Reduction formulas for distribution functions, such as (2.16) or (2.17), are of course useful not only conceptually, but for computational purposes as well. To this end, they may be coupled to any of a number of sequential interrelations between distribution functions, which they then serve to truncate. Since our objective is to analyze the changes in bulk properties evoked by the appearance of a drastic inhomogeneity, it is appealing to seek a formulation in which only bulk properties enter as input, i.e., in which simultaneous use of the (in principle redundant) interaction potential is not required. One such interaction-independent relation has been used several times.[4,6] It relates specifically to the effect of applying an external potential to a system whose internal interactions are all translation invariant. Suppose that $T_\mathbf{a}$ is the finite translation operator

$$T_\mathbf{a} \mathbf{r}_i = \mathbf{r}_i + \mathbf{a}, \qquad \text{any } i \tag{3.1}$$

Now if $\rho(\mathbf{r})$ is the microscopic density

$$\rho(\mathbf{r}) = \sum \delta(\mathbf{r} - \mathbf{r}_i) \tag{3.2}$$

H_0 the internal Hamiltonian, μ the chemical potential, Ω the grand potential, and

$$U = \sum u(\mathbf{r}_i) \tag{3.3}$$

the external potential, we have in a grand ensemble

$$n(\mathbf{r}|\{u(\mathbf{y})\}) = \text{Tr}\,\rho(\mathbf{r})\exp[-\beta(H_0 + U - N\mu - \Omega)] \tag{3.4}$$

Hence

$$\begin{aligned} n(\mathbf{r} + \mathbf{a}|\{u(\mathbf{y})\}) &= \text{Tr}\,\rho(\mathbf{r} + \mathbf{a})\exp[-\beta(H_0 + U - N\mu - \Omega)] \\ &= \text{Tr}\,T_{\mathbf{a}}^{-1}\rho(r)T_{\mathbf{a}}\exp[-\beta(H_0 + U - N\mu - \Omega)] \\ &= \text{Tr}\,\rho(\mathbf{r})\exp[-\beta(H_0 + T_{\mathbf{a}}UT_{\mathbf{a}}^{-1} - N\mu - \Omega)] \\ &= n(r)|\{u(\mathbf{y} + \mathbf{a})\}) \end{aligned} \tag{3.5}$$

the obvious statement that translating u by $\mathbf{a}$ has the result of translating n by $\mathbf{a}$. The effect of an infinitesimal translation follows immediately by applying $\nabla_{\mathbf{a}}|_{\mathbf{a}=0}$:

$$\nabla n(\mathbf{r}) = \int \nabla u(\mathbf{y})\,\frac{\delta n(\mathbf{r})}{\delta u(\mathbf{y})}\,d\mathbf{y} \tag{3.6}$$

which with its inverse

$$\nabla u(\mathbf{r}) = \int \nabla n(\mathbf{y})\,\frac{\delta u(\mathbf{r})}{\delta n(\mathbf{y})}\,d\mathbf{y} \tag{3.7}$$

are our basic relations.

For a classical system, the change of the one-particle density with an infinitesimal change of external potential is simple and well known:

$$\delta n(1) = -\int \hat{F}_2(1, 2)\,\delta\beta u(2)\,d2 \tag{3.8}$$

where

$$\hat{F}_2(1, 2) \equiv n_2(1, 2) - n(1)n(2) + n(1)\,\delta(1, 2)$$

$\mathbf{x}_1$ being replaced by the short-hand notation 1, etc. The inverse of (3.8) is normally written as

$$\delta\beta u(1) = -\int \hat{C}_2(1, 2)\,\delta n(2)\,d2 \tag{3.9}$$

where

$$\hat{C}_2(1, 2) \equiv \frac{\delta(1, 2)}{n(1)} - c_2(1, 2)$$

c_2 being the direct correlation function of Ornstein and Zernike. Hence (3.6) and (3.7) transcribe to

$$\nabla n(1) + n(1)\beta \nabla u(1) + \int [n_2(1, 2) - n(1)n(2)]\beta \nabla u(2)\, d2 = 0 \quad (3.10a)$$

$$\frac{\nabla n(1)}{n(1)} + \beta \nabla u(1) = \int c_2(1, 2) \nabla n(2)\, d2 \quad (3.10b)$$

either of which is complete providing $n_2(1, 2)$ or $c_2(1, 2)$, respectively, can be supplied from without. These are, however, just first members of hierarchies which are appropriate to the insertion of information about higher correlations. For example, one sequence that extends (3.10a) can be generated by taking the coefficient of $a_{\alpha_1} \cdots a_{\alpha_s}$ in (3.5) (where a_α denotes the α component of **a**), or equivalently by repeated differentiation of (3.6) in the recursive form

$$\nabla_{\alpha_1} \cdots \nabla_{\alpha_{s+1}} n(1) = \int [-\beta \nabla_{\alpha_{s+1}} u(s + 1)] \frac{\delta}{\delta - \beta u(s + 1)} \nabla_{\alpha_1} \cdots \nabla_{\alpha_s} n(1)\, d_{s+1} \quad (3.11)$$

This yields in short order

$$\nabla_\alpha n(1) = \int [-\beta \nabla_\alpha u(2)] \hat{F}_2(12)\, d2$$

$$\nabla_{\alpha_1} \nabla_{\alpha_2} n(1) = \int [-\beta \nabla_{\alpha_1} u(2)][-\beta \nabla_{\alpha_2} u(3)] \hat{F}_3(123)\, d2\, d3$$

$$+ \int [-\beta \nabla_{\alpha_1} \nabla_{\alpha_2} u(2)] \hat{F}_2(12)\, d2 \quad (3.12)$$

$$\nabla_{\alpha_1} \nabla_{\alpha_2} \cdots \nabla_{\alpha_s} n(1) = \int \cdots \int \sum_{t=2}^{s+1} (-\beta)^{t-1}$$

$$\times \sum_{\sum A_i = (1, \ldots, s)} \prod_{i=2}^{t} \left[\prod_{j \in A_i} \nabla_{\alpha_j} \right] u(i) \hat{F}_t(1, \ldots, t)\, d2 \cdots dt$$

where the disjoint subsets A_i are ordered, $A_i < A_{i+1}$, using any convenient subset ordering; here

$$\hat{F}_t(1, \ldots, t) = \delta \hat{F}_{t-1}(1, \ldots, t - 1)/\delta - \beta u(t)$$

is the tth-order modified Ursell function.

Equation (3.10b) can of course be extended in precisely the same way. Applying the above procedure to $\ln n(1) + \beta u(1)$, we generate the sequence starting with

$$\nabla[\ln n(1) + \beta u(1)] = \int c_2(12)\, \nabla n(2)\, d2$$

$$\nabla_{\alpha_1}\nabla_{\alpha_2}[\ln n(1) + u(1)] = \int c_3(123)\, \nabla_{\alpha_1} n(2)\, \nabla_{\alpha_2} n(3)\, d2\, d3 + \int c_2(12)\, \nabla_{\alpha_1}\nabla_{\alpha_2} n(2)\, d2 \tag{3.13}$$

where $c_3(123) = \delta c_2(12)/\delta n(3)$ is the third direct correlation, etc. Other hierarchies [in fact implying (3.12), (3.13)] can be obtained by functional differentiation of (3.10). Equivalently, for (3.10a), we can employ an infinitesimal translation in the now obvious

$$n_s(\mathbf{r}_1 + \mathbf{a},\ldots, \mathbf{r}_s + \mathbf{a} | \{u(y)\}) = n_s(\mathbf{r}_1,\ldots, \mathbf{r}_s | \{u(\mathbf{y} + \mathbf{a})\}) \tag{3.14}$$

resulting in

$$(\nabla_1 + \cdots + \nabla_s) n_s(1,\ldots, s) = \int \frac{\delta n_s(1,\ldots, s)}{\delta u(s+1)} \nabla u(s+1)\, ds+1 \tag{3.15}$$

or via standard functional derivative operations,

$$(\nabla_1 + \cdots + \nabla_s) n_s(1,\ldots, s) + n_s(1,\ldots, s)\beta \sum u(j) + \int [n_{s+1}(1,\ldots, s+1) - n_s(1,\ldots, s) n(s+1)]\, \nabla u(s+1)\, ds+1 = 0 \tag{3.16}$$

Similarly, from

$$c_s(\mathbf{r}_1 + \mathbf{a},\ldots, \mathbf{r}_s + \mathbf{a} | \{n(y)\}) = c_s(\mathbf{r}_1,\ldots, \mathbf{r}_s | \{n(\mathbf{y} + \mathbf{a})\}) \tag{3.17}$$

we can generate the sequence

$$(\nabla_1 + \cdots + \nabla_s) c_s(1,\ldots, s) = \int c_{s+1}(1,\ldots, s+1)\, \nabla n(s+1)\, ds+1 \tag{3.18}$$

which includes (3.10b) when one makes the identification $c_1(\mathbf{r}) = \ln n(\mathbf{r}) + \beta u(\mathbf{r})$.

Finally, it should be noted that the development of this section goes through unchanged for any infinitesimal transformation under which the internal Hamiltonian is invariant. For example, for rotational invariance, we need the operator

$$\mathbf{L} = \mathbf{r} \times \nabla \tag{3.19}$$

and thereby obtain

$$\frac{\mathbf{L}n(1)}{n(1)} + \beta\mathbf{L}u(1) = \int c_2(1, 2)\mathbf{L}n(2)\, d2 \tag{3.20}$$

which is not derivable from (3.10b), and in fact may be combined with (3.10b) to yield

$$\int c_2(1, 2)(\mathbf{r}_1 - \mathbf{r}_2) \times \nabla n(2)\, d2 = 0 \tag{3.21}$$

The operators ∇ and $\mathbf{L}$ can be combined in forming higher order derivative relations analogous to (3.12), (3.13).

Now, how are the various hierarchies to be used? In practice, they must be terminated with some approximation. Let us consider the first member (3.10a) to illustrate the type of problem encountered. For definiteness, suppose that u represents a hard wall $z \leqslant 0$ (meaning that particle *centers* cannot penetrate this region). Then

$$\begin{aligned} n(\mathbf{r})\beta\, \nabla u(\mathbf{r}) &= -\{n(\mathbf{r}) \exp[\beta u(\mathbf{r})]\}\, \nabla \exp[-\beta u(\mathbf{r})] \\ &= -\{n(r) \exp[\beta u(\mathbf{r})\}\hat{z}\, \delta(z) = -n_w \hat{z}\, \delta(z) \end{aligned}$$

where n_w is the wall density, and we have used the continuity of $ne^{\beta u}$ in a singular potential. Since the density will be only z dependent, we have from (3.10a)

$$\frac{\partial n(1)}{\partial z_1} = n_w\, \delta(z_1) + n_w \int [n(1|2) - n(1)]_{z_2=0}\, d^2x_2 \tag{3.22a}$$

$$= n_w\, \delta(z_1) + n_w n(1) \int [g(1, 2) - 1]_{z_2=0}\, d^2x_2 \tag{3.22b}$$

the integrand having been reduced by writing $n(1, 2) = n(1|2)n(2)$ and simplifying $n(2)\beta\, \nabla u(2)$ as above. Here and henceforth, the transverse coordinates will be designated by $\mathbf{x} \equiv (x, y)$. "Termination" now consists of expressing $n(1|2)$ or $g(1, 2)$ in terms of known, e.g., bulk quantities.

Any approximations used in (3.22) have at the very least to satisfy a simple restriction: the density must go from the wall density n_w at the wall to the bulk density n_0 as $z \to \infty$. If (3.22) are taken over the full space, they will be consistent with $n(z) = 0$ for $z < 0$, rising to n_w at $z = 0^+$. But the asymptotic bulk density n_0 is not guaranteed. Divide (3.22b) by $u(1)$ and integrate from $z_1 = 0^+$ to ∞, obtaining

$$\ln n_0 - \ln n_w = n_w \int_0^\infty\!\!\int [g(1, 2) - 1]_{z_2=0}\, d^2x_2\, dz_1 \tag{3.23}$$

If $g(1, 2)$ is replaced by its bulk value $g_0(1, 2)$ and the compressibility relation

$$1 + n_0 \int [g(\mathbf{r}_{12}) - 1]\, d^3r_{12} = \partial n_0/\partial \beta P \tag{3.24}$$

utilized, (3.23) yields the approximation

$$\ln(n_0/\beta P) \simeq \tfrac{1}{2}(\beta P/n_0)(\partial n_0/\partial \beta P - 1) \tag{3.25}$$

which is simply not true. If instead the kernel of (3.22a) in the region $z_1 > 0$ is replaced by its bulk value $n_0[g_0(\mathbf{r}_{12}) - 1]$ and we integrate from 0^+ to ∞, there results

$$\frac{n_0}{\beta} - 1 = \frac{1}{2}\left(\frac{\partial n_0}{\partial \beta P} - 1\right) \tag{3.26}$$

which is different but still not correct [it implies $n_0 = \beta P - c(\beta P)^{1/2}$].

The situation is not improved if the kernel of (3.22a) is replaced by the shielding approximation

$$n(1|2) - n(1) = n_0 g_0(\mathbf{r}_{12}) - n(1) \tag{3.27}$$

which is guaranteed to work in one dimension (for nearest neighbor forces). In the three-dimensional version, what is produced is not just a poor approximation, but in fact a divergent integral. The reason for this is instructive. As we have pointed out, the shielding approximation is not valid for large transverse separation of $\mathbf{r}_1$ and $\mathbf{r}_2$, where indeed $n(1|2) - n(1)$ is seen to approach $n_0 - n(1)$ instead of the correct value of zero.

It is a bit unfair to assume that $n(z)$ vanishes for $z < 0$ and then look only at the interval 0^+ to ∞: the hard wall is but a convenient test potential, and the vanishing of $n(z)$ within it should be an automatic consequence of the theory. To examine this point, let me return to (3.10b), which, in the context of approximate truncations, need not be equivalent to (3.10a). Again, we set $n(\mathbf{r})\, \nabla\beta u(\mathbf{r}) = -n_w \hat{z}\, \delta(z)$, for which purpose (3.10b) is first multiplied by $n(1)$:

$$n'(z_1) = n_w\, \delta(z_1) + \int n(z_1) c_2(1, 2) n'(z_2)\, d2 \tag{3.28}$$

Now if the kernel replacement $c_2(1, 2) \to c_{20}(r_{12})$ is made, $n(z)$ will vanish for z < 0, but the system cannot be solved in closed form and $n - n_0$ will again be incorrect. If, instead, $n(z_1)c_2(1, 2) \to n_0 c_{20}(\mathbf{r}_{12})$, $n(z)$ will only vanish up to minus the range of c_2, and of course $n_w - n_0$ will be incorrect. The former deficiency can be corrected by replacing $n_w\, \delta(z_1)$ by a function vanishing for $z_1 < 0$ [so that ∇u in (3.10b) remains infinite for $z_1 < 0$, zero for $z_1 > 0$] so constructed that $n(z) = 0$ for $z_1 < 0$. This gives an excellent hard-core density profile[9] except near the wall, but of course the balance between wall density and asymptotic density is not maintained. Various ad hoc strategies can be used to correct the wall contact region, but their basic empirical nature leaves something to be desired.

4. DYNAMIC HIERARCHY

One of the reasons for the difficulty with (3.10) is, as we have noted, that it requires complete transverse information on $n_2(1, 2) - \mathbf{x}_2$ covers all of space. This requires good matching between short- and long-range correlations, and implies that any unsuspected long-range order, e.g., near a phase transition, will be missed in any obvious approximation. It also means that the limited transverse extension needed for the shielding approximation does not obtain (but see Section 9). This objection becomes less compelling when the correlation range is far exceeded by the interaction range, as in Coulomb forces, but that is another story.

Let us suppose then that we are considering a system with short-range interaction. To take advantage of this, we require a formulation in which the interaction appears as an explicit weight. The required input of consistent interaction potential and bulk distribution data is not that onerous, as we shall see. This suggests that we examine the use of the grandaddy of distribution hierarchies, the BBGKY system (see, e.g., Ref. 16). This can in fact be derived as we did (3.6), with two modifications, as follows.

First, we must now consider spatial transformations under which the internal Hamiltonian H_0 is not invariant, and second, with this added generality, it suffices to examine the change in the "0-particle" quantity $\Xi = e^{-\beta\Omega}$, the grand partition function, i.e.,

$$\Xi = \mathrm{Tr}\exp[-\beta(H_0 + U - Nu)] \tag{4.1}$$

We will also assume hereafter that the internal potential is due only to pairwise interactions:

$$H_0 = K + \Phi, \qquad K = \sum p_i^2/2m, \qquad \Phi = \frac{1}{2}\sum_{i\neq j} \phi(\mathbf{r}_i, \mathbf{r}_j) \tag{4.2}$$

Restricting our attention now to the classical case, we carry out a pure spatial distortion T which is not volume-preserving. Since

$$d^3(T\mathbf{r}T^{-1}) = \mathrm{Det}\,\nabla T(\mathbf{r})\, d^3r = \exp[\mathrm{Tr}\ln \nabla T(r)]\, d^3r \tag{4.3}$$

we now have

$$\Xi = \mathrm{tr}\exp\left(-\beta\left\{\mathrm{TH_0T^{-1}} + \mathrm{TUT^{-1}} - \frac{1}{\beta}\mathrm{Tr}\sum_i \ln[\nabla T(\mathbf{r}_i)] - N\mu\right\}\right) \tag{4.4}$$

The corresponding infinitesimal δT has the general form

$$\delta T f(\mathbf{r}_i) = \xi(i) \cdot \nabla f(\mathbf{r}_i) \tag{4.5a}$$

so that

$$\begin{aligned} [\delta T, u(i)] &= \xi(i) \cdot \nabla u(i) \\ [\delta T, \phi(i, j)] &= [\xi(i) \cdot \nabla_i + \xi(j) \cdot \nabla_j] \phi(i, j) \\ \operatorname{Tr} \ln[\mathbf{V}(\mathbf{r}_i + \delta T(\mathbf{r}_i)] &= \nabla \cdot \xi(i) \end{aligned} \tag{4.5b}$$

Hence the infinitesimal version of (4.4) reads

$$\begin{aligned} 0 = \int \nabla \cdot \xi(1) n(1) \Xi \, d1 &+ \int \xi(1) \cdot \nabla u(1) \, \delta\Xi/\delta u(1) \, d1 \\ &+ \iint [\xi(1) \cdot \nabla_1 + \xi(2) \cdot \nabla_2] \phi(1, 2) \, \delta\Xi/\delta\phi(1, 2) \, d1 \, d2 \end{aligned} \tag{4.6}$$

On taking the coefficient of $\xi(1)$ [applying $\delta/\delta\xi(1)$], we find that (4.6) reduces at once to

$$\nabla n(1) + n(1)\beta \, \nabla u(1) + \int n_2(1, 2)\beta \, \nabla_1 \phi(1, 2) \, d2 = 0 \tag{4.7}$$

the first of the BBGKY hierarchy. But this formal derivation conceals the physical significance of (4.7). Let us start instead with the basic Newton equations for the balance of momentum flow

$$m\ddot{\mathbf{r}}_i = -\nabla u(\mathbf{r}_i) = \sum_{j \neq i} \nabla_i \phi(\mathbf{r}_i, \mathbf{r}_j) \tag{4.8}$$

and using a test function $\xi(\mathbf{r})$, convert these to

$$m \sum \xi(\mathbf{r}_i) \cdot \ddot{\mathbf{r}}_i = -\sum \xi(\mathbf{r}_i) \cdot \nabla u(\mathbf{r}_i) - \sum_{j \neq i} \xi(\mathbf{r}_i) \cdot \nabla_i \phi(\mathbf{r}_i, \mathbf{r}_j) \tag{4.9}$$

Now on averaging in classical equilibrium

$$\langle \xi(\mathbf{r}_i) \cdot \ddot{\mathbf{r}}_i \rangle = -\left\langle \frac{d}{dt} \xi(\mathbf{r}_i) \cdot \dot{\mathbf{r}}_i \right\rangle = -\langle \dot{\mathbf{r}}_i \cdot \nabla \xi(\mathbf{r}_i)] \cdot \dot{\mathbf{r}}_i \rangle = -\frac{1}{m\beta} \langle \nabla \cdot \xi(\mathbf{r}_i) \rangle$$

so that

$$\begin{aligned} \frac{1}{\beta} \int n(1) \nabla \cdot \xi(1) \, d1 = \int & \nabla u(1) \cdot \xi(1) n(1) \, d1 \\ &+ \iint \xi(1) \cdot \nabla_1 \phi(1, 2) n_2(1, 2) \, d1 \, d2 \end{aligned} \tag{4.10}$$

the "hypervirial" generalization of the virial theorem, which involves the choice $\xi(1) = \mathbf{r}_1$. On applying $\delta/\delta\xi(1)$. we recover (4.7), which can thus be identified with the local conservation of momentum flow. [Somewhat more briefly, (4.7) is an immediate consequence of the general sum rule $\langle \nabla \cdot \mathbf{F} + \mathbf{F} \cdot \nabla \beta(\Phi + U) \rangle = 0$ with the dynamical origin $\langle [H, \mathbf{p} \cdot \mathbf{F}] \rangle = 0$.]

An important virtue of (4.7) is that consistency between wall density and asymptotic density for a wall-bounded fluid is guaranteed. In the presence of a hard wall, (4.7) transcribes as before to

$$\nabla n(1) + \int n_2(1,2)\, \nabla_1 \beta\phi(1,2)\, d2 = n_w\, \delta(z_1)\hat{z} \tag{4.11}$$

resulting of course in a rise of $n(1)$ from zero to n_w as the wall is passed. But in addition, the implicit momentum flow conservation produces asymptotic consistency: multiply by the unit step function $\epsilon(z - z_1)$ and integrate over all z_1, obtaining

$$n_w - n(z) = \frac{1}{2} \int n_2(1,2)[\epsilon(z - z_1) - \epsilon(z - z_2)] \times \frac{\partial}{\partial z_1} \beta\phi(1,2)\, dz_1\, dz_2\, d^2x_1 \tag{4.12}$$

This is precisely the virial theorem for pressure if $n_2(1, 2)$ reduces to its bulk value for large z_1, z_2, which is thereby the only condition needed.

The sharp distinction between the dynamic BBGKY equation (4.7) and the kinematic linear response equation (3.10a) is of course illusory. They both stem from examination of the change of distribution functions under spatial transformations. But the linear response format uses only special Hamiltonian-preserving transformations and so must employ a higher distribution to convey the same amount of information. To see this explicitly, let us restrict ξ in (4.6) to the constant unit dyadic I. We then have

$$0 = -\beta \int n(1)\, \nabla u(1)\, d1 - \tfrac{1}{2}\beta \int (\nabla_1 + \nabla_2)\phi(1,2) n_2(1,2)\, d1\, d2 \tag{4.13}$$

The second term vanishes if $\phi(1, 2)$ is translation invariant, leading to

$$\int n(1)\, \nabla u(1)\, d1 = 0 \tag{4.14}$$

Physically, (4.14) asserts that the total external force on the system vanishes. But it may also be recognized as the generator of the linear response sequence (3.15) [multiply by Ξ and differentiate successively with respect to $\delta/\delta e^{-\beta u(2)} \cdots \delta/\delta \epsilon^{-\beta u(s+1)}$] or of (3.18) [differentiate successively with respect to $\delta/\delta n(2) \cdots \delta/\delta n(s + 1)$].

The possible inadequacies of (4.14) or its consequences are apparent from the fact that it is also equivalent to integrating (4.7) over $\mathbf{r}_1$. One therefore no longer has pointwise momentum conservation, but rather a much weaker global statement. The same comment applies to higher members of the hierarchy. To obtain these, first replace ξ in (4.6) by $\xi e^{\beta u}$, yielding

$$0 = \int [\nabla \cdot \xi(1)] n(1) e^{\beta u(1)} \Xi \, d1 - \beta \iint [\xi(1) \cdot \nabla_1 \phi(1, s+1)] \times e^{-\beta u(s+1)} n_2(1, s+1) e^{\beta[u(1)+u(s+1)]} \Xi \, d1 \, ds+1 \tag{4.15}$$

Then differentiate successively $\delta/\delta e^{-u(2)} \cdots \delta/\delta e^{-u(s)}$, so that

$$\begin{aligned} 0 = &\int [\nabla \cdot \xi(1)] n_s(1,\ldots,s) \left[\exp \beta \sum_1^s u(2)\right] \Xi d1 \\ &- \beta \iint \xi(1) \cdot \nabla_1 \phi(1, s+1) \exp[-\beta u(s+1)] \\ &\times n_{s+1}(1,\ldots,s+1) \left[\exp \beta \sum_1^{s+1} u(i)\right] \Xi \, d1 \, ds+1 \\ &- \beta \sum_{j=2}^{s} \int \xi(1) \cdot \nabla_1 \phi(1, i) n_s(1,\ldots,s) \exp[\beta_1{}^s u(i)] \Xi \, d1 \end{aligned} \tag{4.16}$$

and replace ξ by $\xi e^{-\beta u}$:

$$\begin{aligned} &\int \nabla \cdot \xi(1) n_s(1,\ldots,s) \, d1 \\ &\quad = \beta \int n_s(1,\ldots,s) \left[\xi(1) \cdot \nabla u(1) + \sum_2^s \xi(1) \cdot \nabla_1 \phi(1, i)\right] d1 \\ &\quad + \beta \iint n_{s+1}(1,\ldots,s+1) \xi(1) \cdot \nabla_1 \phi(1, s+1) \, d1 \, ds+1 \end{aligned} \tag{4.17}$$

Taking the coefficient of $\xi(1)$ now results in our first option,

$$\begin{aligned} &\nabla_1 n_s(1,\ldots,s) + \beta n_s(1,\ldots,s) \left[\nabla u(1) + \sum_2^s \nabla_1 \phi(1, i)\right] \\ &\quad + \beta \int n_{s+1}(1,\ldots,s+1) \, \nabla_1 \phi(1, s+1) \, ds+1 = 0 \end{aligned} \tag{4.18}$$

the full BBGKY hierarchy.

Cyclical permutation of $1,\ldots,s$ and summation of (4.18) also produces the version analogous to (3.15),

$$\sum_1^s \nabla_i n_s(1,\ldots,s) + \beta n_s(1,\ldots,s) \sum \nabla u(i) + \beta n_s(1,\ldots,s)$$

$$\times \sum_{i \neq j} \nabla_i \phi(i,j) + \beta \int n_{s+1}(1,\ldots,s+1) \sum_i \nabla_i(i,s+1)\, ds + 1 = 0 \qquad (4.19)$$

in which $\sum_{i \neq j} \nabla_i \phi(i,j) = 0$ for translation-invariant ϕ. But then there is the second option: choose $\xi = 1$ in (4.17), equivalent to integrating (4.18) over $\mathbf{r}_1$. If ϕ is translation invariant, then

$$\int n_s(1,\ldots,s)\, \nabla u(1)\, d1 = \int n_s(1,\ldots,s) \sum_2^s \nabla_i \phi(1,i)\, d1 = 0 \qquad (4.20)$$

or reinserting (4.19) for $s \to s-1$,

$$\sum_2^s \nabla_i n_{s-1}(2,\ldots,s) + \beta n_{s-1}(2,\ldots,s) \sum_2^3 \nabla u(i) \beta \int n_s(1,\ldots,s)\, \nabla u(1)\, d1 = 0 \qquad (4.21)$$

precisely the sequence (3.16).

We conclude that the linear response type hierarchy corresponds to an averaged version of the BBGKY sequence, with the attendant advantage of not needing the internal potential but the disadvantage of not satisfying important conservation conditions automatically. More to the point from our present view, however, we have, instead of the relatively short-range Ursell correlations, the variable $\mathbf{r}_{s+1}$ in (4.19) controlled by $\nabla\phi(1, s+1)$, so that indeed the transverse extension of the distributions can be bounded. Thus, a shielded distribution approximation becomes feasible for truly short-range forces and will be used.

5. HARD-SPHERE FLUID BOUNDED BY A HARD WALL

Let us examine the first of the BBGKY hierarchy in further detail for a fluid bounded by a planar hard wall. Since wall density and asymptotic density are automatically correct, we will be interested in how well the intervening density profile can be obtained. For this purpose, we make the aforementioned approximation that the particle closest to the wall in $n_2(1,2)$ effectively shields its partner from the action of the wall. The wall influence of course "leaks through" increasingly as the particles separate, especially transversely, but at least their separation is bounded by the range of the interaction. Thus

$$n_2(1,2) \approx [n(1)\epsilon(z_2 - z_1) + n(2)\epsilon(z_1 - z_2)] n_0 g_0(1\text{–}2) \qquad (5.1)$$

and (4.11) reduces to

$$\frac{\partial n(z_1)}{\partial z_1} + n_0 \int [n(z_1)\epsilon(z_2 - z_1) + n(z_2)\epsilon(z_1 - z_2)] \frac{z_{12}}{r_{12}} g_0(r_{12})\beta\phi'(r_{12})\, dz_2\, dx_2{}^2 = \beta P\, \delta(z_1) \quad (5.2)$$

Since

$$\int f(r_{12})\, dx_2{}^2 = \int f[(z_{12}^2 + \rho^2)^{1/2}] 2\pi\rho\, d\rho = \pi \int_{z_{12}}^{\infty} f(R)\, d(R^2) = 2\pi \int_{z_{12}}^{\infty} Rf(R)\, dR$$

and the coefficient of $n(z_1)\epsilon(z_1 - z_2)$ in the integrand is odd in z_{12}, we have

$$\frac{\partial n(z_1)}{\partial z_1} + 2\pi n_0 \int u(z_2)\epsilon(z_1 - z_2) z_{12} \int_{z_{12}}^{\infty} g_0(R)\beta\phi'(R)\, dR\, dz^2 - 2\pi n_0 n(z_1) \int \epsilon(z_1 - z_2) z_{12} \int_{z_{12}}^{\infty} g_0(R)\beta\phi'(R)\, dR\, dz_2 = \beta P\, \delta(z_1) \quad (5.3)$$

Equation (5.3) is a linear equation in $n(z_1)$ which can be solved by applying the Fourier transform $\int (\cdot) e^{ikz_1}\, dz_1$:

$$-ik\tilde{n}(k) + 2\pi n_0 \tilde{n}(k) \int_0^{\infty} e^{ikz} z \int_z^{\infty} g_0(R)\beta\phi'(R)\, dR\, dz - 2\pi n_0 \tilde{n}(k) \int_0^{\infty} z \int_z^{\infty} g_0(R)\beta\phi'(R)\, dR\, dz = \beta P \quad (5.4)$$

or

$$\tilde{n}(k) = \frac{\beta P}{-ik + n_o[f_1(k) - f_1(0)]} \quad (5.5)$$

where

$$f_1(k) \equiv 2\pi \int_0^{\infty} g_0(z)\beta\phi'(z) \frac{\partial}{\partial k}\left(\frac{1 - e^{ikz}}{k}\right) dz$$

$\tilde{n}(k)$ of course denotes the Fourier transform of $n(z)$. Note that the condition

$$n_0 = n(z)|_{-\infty}^{\infty} = \lim_{k \to 0} [-ik\tilde{n}(k)] = \beta P/[1 + in_0 f_1{}'(0)]$$

or

$$n_0 = \beta P \Big/ \left[1 - \tfrac{2}{3}\pi n_0 \int_0^\infty z^3 g_0(z) \beta\phi'(z)\, dz \right] \tag{5.6}$$

is just the virial theorem equation of state.

Let us first look at the case of pure hard-sphere particles of diameter a. Then

$$g_0(z)\beta\phi'(z) = -[g_0(z)e^{\beta\phi(z)}][e^{-\beta\phi(z)}]' = -g_a\,\delta(z-a) \tag{5.7}$$

where g_a is the contact value of the radial distribution. Hence

$$\begin{aligned} f_1(k) &= -2\pi g_a \frac{\partial}{\partial k}\frac{1-e^{ika}}{k} = 2\pi g_a\left[\frac{1}{k^2} + \left(\frac{ia}{k} - \frac{1}{k^2}\right)e^{ika}\right] \\ f_1(0) &= -\pi a^2 g_a \end{aligned} \tag{5.8}$$

and

$$\begin{aligned} \tilde{n}(k) = \beta P\bigg[&-ik + n_0\pi a^2 g_a\left(1 + \frac{2}{k^2a^2}\right) \\ &+ 2\pi n_0 g_a a^2\left(\frac{i}{ka} - \frac{1}{k^2a^2}\right)e^{ika}\bigg]^{-1} \end{aligned} \tag{5.9}$$

On reverse Fourier transforming, and setting $t = -ika$, we have

$$n(za) = \frac{\beta P}{2\pi}\int_{-i\infty}^{i\infty} \frac{e^{tz}\,dt}{t + a^2 n_0 g_a(1 - 2/t^2) + 2\pi a^2 n_0 g_a(1/t + 1/t^2)e^{-t}} \tag{5.10}$$

where g_a is determined, via (5.6), by

$$\beta P = n_0(1 + \tfrac{2}{3}\pi n_0 a^3 g_a) \tag{5.11}$$

Equation (5.10) must be evaluated numerically, a process that is greatly facilitated by rewriting first as

$$n(za) = \frac{\beta P}{2\pi n_0 a^3 g_a}\frac{-1}{2\pi i}\int \frac{t^2 e^{tz}\,dt}{D(t) - (1+t)e^{-t}} \tag{5.12}$$

where

$$D(t) = 1 - \tfrac{1}{2}t^2 - Kt^3, \qquad K = 1/2\pi n_0 a^3 g_a$$

and then as

$$\begin{aligned} n(za) = \frac{-\beta PK}{2\pi i}&\int_{c_1} \frac{t^2e^{tz}\{1 - [(1+t)e^{-t}/D(t)]^{1+[za]}\}}{D(t) - (1+t)e^{-t}}\,dt \\ \frac{-\beta PK}{2\pi i}&\int_{c_2} \frac{t^2e^{tz}[(1+t)e^{-t}/D(t)]^{1+[za]}}{D(t) - (1+t)e^{-t}}\,dt \end{aligned} \tag{5.13}$$

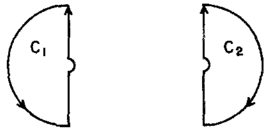

Fig. 2. Contours for Eq. (5.13).

Here the path from $-i\infty$ to $i\infty$ is closed by an infinite semicircle, with $\operatorname{Re} t \leqslant 0$ for C_1, $\operatorname{Re} t \geqslant 0$ for C_2, and the origin avoided in each case by a small semicircle $\operatorname{Re} t \geqslant 0$. Then C_1 can be contracted to a circle C_1' centered on the real axis, and containing the origin and the two negative real roots of $D(t) = 0$, and C_2 to a circle C_2' surrounding just the positive real root of $D(t) = 0$ (Fig. 2). It is of course important to observe (for C_2) that $D(t) - (1 + t)e^{-t} \neq 0$ for $\operatorname{Re} t \geqslant 0$ except at $t = 0$, which a little algebra accomplishes.[2] Numerical integration over C_1' and C_2' is then easy and accurate.

Two more points must be noted in practice.[(9)] First is that numerical simulation of an equilibrium fluid requires not one, but two walls, to keep the system finite. This requires a source term $n_w[\delta(z) + \delta(L - z)]$ to replace $n_w\, \delta(z)$ in (4.11), but it is now the nearest wall that is shielded in (5.2). If the pattern $n(z) - n_0$ has, however, decayed by the position L of the second wall, then it suffices to make the replacement

$$n(z) \to n(z) + n(L - z) - n_0 \tag{5.14}$$

and we shall do so.

Second, in the same numerical experiments, it is the mean density in the box from 0 to L that is fixed, not the asymptotic bulk density, which must thereby be computed. But if L is greater than the scale of the profile $[n(z) - n_0 \sim 0$ at $z \sim L$, as above], the relation is readily found:

$$\begin{aligned} \bar{n} &= \frac{1}{L} \int_0^L [n(z) + n(L - z) - n_0]\, dz = n_0 + \frac{2}{L} \int_0^L [n(z) - n_0]\, dz \\ &\sim n_0 + \frac{2}{L} \int_0^\infty [n(z) - n_0]\, dz = n_0 + \frac{2}{L} \lim_{k \to 0} \int_0^\infty e^{ikz}[n(z) - n(0)]\, dz \end{aligned}$$

---

[2] If $I(t) \equiv (1 + t)e^{-t} - 1 + \frac{1}{2}t^2 + Kt^3$, then $I(0) = 0$ and

$$I'(t) = t^2[3K + (1 - e^{-t})/t]$$

Hence if $t = u + iv = Re^{i\theta}$,

$$e^{-3i\theta} I(t) = \int_0^R \rho^2 \left[3K + \int_0^1 e^{\alpha(\rho/R)(u + iv)}\, d\alpha \right] d\rho$$

But

$$R_e \int_0^1 e^{\alpha(\rho/R)(u+iv)}\, d\alpha = \int_0^1 e^{\alpha(\rho/R)u} \cos\left(\alpha \frac{\rho}{R} v\right) d\alpha \geqslant 0 \qquad \text{for} \qquad u \geqslant 0$$

and so $I(t) \neq 0$.

or

$$\bar{n} = n_0 + \frac{2}{L} \lim_{k \to 0} \left[n(k) - \frac{i n_0}{k} \right] \tag{5.15}$$

For (5.9), this reduces to

$$\bar{n} = n_0 + \frac{3}{4L} n_0 a \frac{\beta P - n_0}{\beta P} \tag{5.16}$$

Given $\bar{n}$, n_0 can now be solved by Newton–Raphson iteration, resulting in the correction sequence

$$n_0' = \left[\left(\frac{\beta P}{n_0} \right)^2 \bar{n} + \frac{3a}{4L} \left(\frac{\partial \beta P}{\partial n_0} - \frac{\beta P}{n_0} \right) \right] \times \left\{ \left(\frac{\beta P}{n_0} \right)^2 + \frac{3a}{4L} \left[\frac{\partial \beta P}{\partial n_0} - 2 \frac{\beta P}{n_0} + \left(\frac{\beta P}{n_0} \right)^2 \right] \right\}^{-1} \tag{5.17}$$

We further choose $\beta P(n)$ empirically via the Carnahan–Starling[17] approximation,

$$\frac{\beta P}{n} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \qquad \frac{\partial \beta P}{\partial n} = \frac{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4}{(1 - \eta)^4} \tag{5.18}$$

where $\eta \equiv \pi n a^3/6$.

In Fig. 3, the profile given by (5.13) and (5.14) is compared with the "experimental" value, i.e., the numerical simulation of Liu.[8] For these data,

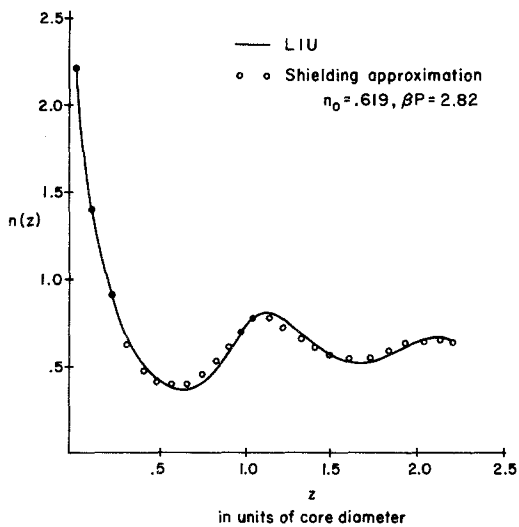

Fig. 3. Hard cores bounded by a wall; comparison of Liu's simulation and the shielding approximation at bulk density $n = 0.619$.

with $L = 4.5a$ and $\bar{n}a^3 = 0.7$, we find from (5.17) and (5.18), $na^3 = 0.619$, $\beta Pa^3 = 2.82$. Comparison of (5.13) with Liu's results shows that quite a good representation is achieved, with some flattening of the peaks and troughs of the profile.

6. FLUID EXTERNAL TO A HARD SPHERE

Let us now generalize our geometry, and imagine the bounding surface to be a spherical inclusion, perhaps the prototype of a large molecule. The curvature now presents us with, among other things, an additional controllable parameter with which to assess our state of knowledge. Suppose then that there is a hard sphere of radius R centered at the origin, and we are examining the fluid density external to the sphere. Since now

$$n(1)\beta\,\nabla u(1) = -n(1)e^{\beta u(1)}\,\nabla e^{-\beta u(1)} = -n_w\,\delta(r_1 - R)\mathbf{r}_1$$

the $\mathbf{r}_1$ component of (4.7) yields

$$\frac{\partial n(r_1)}{\partial r_1} + \int n_2(1,2)\frac{r_1 - r_2\cos\theta}{r_{12}}\,\beta\phi'(r_{12})\,d2 = n_w\,\delta(r_1 - R) \qquad (6.1)$$

where θ is the angle of $\mathbf{r}_2$ with respect to $\mathbf{r}_1$. The shielding approximation used in (5.1) must now be replaced by

$$n_2(1,2) \approx [n(r_1)\epsilon(r_2 - r_1) + n(r_2)\epsilon(r_1 - r_2)]n_0 g_0(r_{12}) \qquad (6.2)$$

Hence, switching from integration coordinates r_2, θ to r_2, r_{12}, we have

$$n'(r_1) + \frac{\pi n_0}{r_1{}^2}\iint_\Delta [n(r_2) - n(r_1)]\epsilon(r_1 - r_2) \times (r_1{}^2 + r_{12}^2 - r_2{}^2)r_2 g_0(r_{12})\beta\phi'(r_{12})\,dr_2\,dr_{12} = n_w\,\delta(r_1 - R) \qquad (6.3)$$

where Δ denotes the triangle relation $|r_2 - r_{12}| \leqslant r_1 \leqslant r_2 + r_{12}$. Assuming that *R exceeds the range of interaction*, this reduces to the single restriction $r_{12} \geqslant |r_1 - r_2|$.

Equation (6.3) can now be handled in standard fashion. Multiply by $r_1{}^2$ and take the one-dimensional Fourier transform. We thus require

$$\pi \iiint_{r_{12}\geqslant r_2 - r_1 \geqslant 0} e^{ikr_1}n(r_1)r_2(r_1{}^2 - r_2{}^2 + r_{12}^2)g_0(r_{12})\beta\phi'(r_{12})\,dr_1\,dr_2\,dr_{12}$$

$$= \pi \iiint_{r \geqslant r_2 \geqslant 0} e^{ikr_1}n(r_1)(r_2 + r_1)(r^2 - r_2{}^2 - 2r_1r_2)g_0(r)\beta\phi'(r)\,dr_1\,dr_2\,dr$$

$$= \left[2\pi\int_0^\infty \tfrac{1}{8}r^4 g_0(r)\beta\phi'(r)\,dr + 2\pi\int_0^\infty \tfrac{1}{2}r^2 g_0(r)\beta\phi'(r)\,dr\,\frac{\partial^2}{\partial k^2}\right]\tilde{n}(k) \qquad (6.4)$$

as well as

$$\pi \iiint_{r_{12}\geqslant r_1 - r_2 \geqslant 0} e^{ikr_1} n(r_2) r_2 (r_1{}^2 - r_2{}^2 + r_{12}^2) g_0(r_{12}) \beta\phi'(r_{12})\, dr_1\, dr_2\, dr_{12}$$

$$= \pi \iiint_{r \geqslant r_1 \geqslant 0} g_0(r)\beta\phi'(r) e^{ikr_1} r_2 (r_1{}^2 + 2r_1 r_2 + r^2) e^{ikr_2} n(r_2)\, dr_1\, dr_2\, dr$$

$$= \pi \iint_{r \geqslant r_1 \geqslant 0} g_0(r)\beta\phi'(r) e^{ikr_1} \times \left[-2r_1 \frac{\partial^2}{\partial k^2} - i(r_1{}^2 + r^2) \frac{\partial}{\partial k} \right] dr\, dr_1\, \tilde{n}(k) \tag{6.5}$$

In terms of

$$f_1(k) = -2\pi \int_0^\infty g_0(r)\beta\phi'(r) \left(\frac{ir}{k} - \frac{1}{k^2} \right) \left(e^{ikr} + \frac{1}{k^2} \right) dr \tag{6.6}$$

of (5.5), (6.4) thus becomes after a little more algebra

$$i \frac{\partial}{\partial k^2} [k\tilde{n}(k)] + n_o [f_1(0) - f_1(k)] \frac{\partial^2}{\partial k^2} \tilde{n}(k) + n_0 \left[\frac{f_1(0) - f_1(k)}{k} - f_1{}'(k) \right] \frac{\partial}{\partial k} \tilde{n}(k) - \tfrac{1}{2} n_0 f_1{}''(0) \tilde{n}(k) = n_w R^2 e^{ikR} \tag{6.7}$$

A convenient form for (6.7) is (after multiplying by k)

$$\frac{\partial}{\partial k} \left[\{ -ik^2 + n_0 k [f_1(k) - f_1(0)] \} \frac{\partial \tilde{n}(k)}{\partial k} \right] + \tfrac{1}{2} n_0 k f_1{}''(0) \tilde{n}(k) = -n_w R^2 k e^{ikr} \tag{6.8}$$

However, the solution of (6.8) is not trivial, and we will concentrate upon two limiting situations. First, suppose that R is large. Then it is certainly preferable to work in terms of density referred to surface:

$$n_w(n) \equiv n(R + r) \tag{6.9}$$

or equivalently

$$\tilde{n}(k) = \tilde{n}_w(k) e^{ikr} \tag{6.10}$$

so that (6.8) now reads

$$\left(1 - \frac{i}{R} \frac{\partial}{\partial k} \right) \left[\{ -ik^2 + n_0 k [f_1(k_1 - f_1(0))] \} \left(1 - \frac{i}{R} \frac{\partial}{\partial k} \right) \right] \tilde{n}_w(k) - \frac{1}{2R^2} n_0 f_1{}''(0) k \tilde{n}_w(k) = n_w k \tag{6.11}$$

or in terms of the plane wall solution $\tilde{n}_\infty(k)$ of (5.5),

$$\left(1 - \frac{i}{R}\frac{\partial}{\partial k}\right)\frac{k}{\tilde{n}_\infty(k)}\left(1 - \frac{i}{R}\frac{\partial}{\partial k}\right)n_w(k) - \frac{1}{2R^2}\frac{n_0}{\beta P} f_1''(0)k\tilde{n}_w(k) = \frac{n_w}{\beta P}k \quad (6.12)$$

For large R, we can drop the second-order terms $1/R^2$ in a perturbation expansion. To this order, we have at once

$$\tilde{n}_w(k) = \frac{n_w}{\beta P}\tilde{n}_\infty(k) - \frac{i}{R}\left(\frac{\partial}{\partial k} + \frac{1}{k}\right)\tilde{n}_\infty(k) \quad (6.13)$$

or reverse Fourier transforming,

$$n_w(r) = \frac{n_w}{\beta P}n_\infty(r) - \frac{1}{R}\int_0^r x n_\infty'(x)\,dx \quad (6.14)$$

Accurate numerical experiments, however, do not yet exist. As a final comment, since $n_\infty(\infty) = n_w(\infty) = n_0$, we find from (6.14)

$$n_w = \frac{\beta P}{n_0}\left[n_0 + \frac{1}{R}\int_0^\infty x n_\infty'(x)\,dx\right] \quad (6.15)$$

The second limit is that of small R. Rewrite (6.8) in the fashion of (6.12):

$$\frac{\partial}{\partial k}\left[\frac{k^2}{k\tilde{n}_\infty(k)}\frac{\partial}{\partial k}\tilde{n}(k)\right] + \left[\frac{\partial}{\partial k}\frac{1}{k\tilde{n}_\infty(k)}\right](0)k\tilde{n}(k) = -\frac{n_w R^2}{\beta P}ke^{ikr} \quad (6.16)$$

and suppose that the particles are pure hard cores of diameter a. In that case, a wall with $R = a$ is just another particle, and

$$n(r; a) = n_0 g_0(r) \quad (6.17)$$

Hence if (6.17) could be solved, it would yield another approximation for the pair distribution function. Although this approximation appears to require βP as input, it also yields

$$\frac{2n_0}{\partial \beta P} = 1 + \left[\tilde{n}(k) - \frac{in_0}{k}\right](0) \quad (6.18)$$

as output, so that βP is available in self-consistent form. There is yet another way of interpreting (6.17) for hard cores with $R = a$, and that is as a model relation between n_∞ and $n = n_0 g$. In other words, we solve (6.17) for n_∞, using

$$\left\{\frac{\partial[k\tilde{n}_\infty(k)]}{\partial k}\right\}(0) = \left\{\frac{\partial}{\partial k}k\left[\tilde{n}_\infty(k) - i\frac{n_0}{k}\right]\right\}(0) = [\tilde{n}_\infty(k) - in_0(k)](0)$$

obtaining

$$\tilde{n}_{\infty}(k) = -\left[k \frac{\partial}{\partial k} \tilde{n}(k)\right] \times \left[1 + \frac{n_w a^2}{\beta P} \int_0^k k e^{ika}\, dk + \left(\tilde{n}_{\infty} - i\frac{n_0}{k}\right)(0) \int_0^k k\tilde{n}(k)\, dk\right]^{-1} \quad (6.19)$$

so that n_{∞} can be formed from any believable g_0. Note, however, that recomputation of $[\tilde{n}_{\infty} - i(n_0/k)](0)$ from (6.19) produces an identity, so that this parameter must be supplied externally.

7. SOFT SPHERES BOUNDED BY A SOFT WALL

We return to the case of a planar wall, but relax the hard-wall character of both the bounding wall and interparticle interaction. If the wall is not hard but instead represents a potential u, we cannot make the replacement $n\, \nabla\beta u \to -n_w\, \delta(z)\hat{z}$ in (4.71). In principle, this poses no difficulty, but it does preclude the solution of (5.3) by simple Fourier transform. Let us suppose, however, that when the wall potential differs from 0 or ∞, it changes rapidly, e.g., a hard wall followed by a deep but narrow attractive wall. Since $ne^{\beta u}$ is continuous together with its derivative even for discontinuous u, the consequent slow variation of $ne^{\beta u}$ allows us to make the approximation

$$n\,\nabla\beta u = -ne^{-\beta u}\,\nabla e^{-\beta u} \simeq -n_w e^{\beta u_w}\,\nabla e^{-\beta u}$$

for any nominal wall position. Since the wall pressure, or wall force per unit area, is given by $P_{\infty} = \int n(\mathbf{r})[-\nabla u(\mathbf{r})]\cdot\hat{z}\, dz$, then in this approximation

$$\beta P = \int_{-\infty}^{\infty} n_w e^{\beta u_w}(e^{-\beta u(z)})'\, dz \simeq -n_w e^{\beta u_w}$$

We conclude that

$$n(z)\,\nabla\beta u(z) \simeq -\beta P\,\nabla e^{-\beta u(z)} \quad (7.1)$$

so that now (5.4) is replaced by

$$\tilde{n}(k) = \frac{\beta P(e^{-\beta u(z)})(k)}{1 + in_0[f_1(k) - f_1(0)]/k} \quad (7.2)$$

Equally well, if $n_h(z)$ is the hard-wall solution of (5.5), $n(z)$ can now be written via the convolution

$$n(z) = \int n_h(z - w)(e^{-\beta u(w)})'\, dw \quad (7.3)$$

which is just a running average with the weight function $(e^{-\beta u(w)})'$.

By virtue of (7.13), we can once more concentrate upon the pure hard-wall case, with

$$(e^{-\beta u(z)})(k) = 1/k \tag{7.4}$$

It should of course be observed that the shielding approximation decreases in accuracy when the wall is sticky, since the resulting particle layer extends the influence of the wall both normally and transversely. At any rate, let us examine the nature of the density profile in the approximation (5.4) or (7.2). For this purpose, it is best to rewrite (5.4) as

$$\tilde{n}_h(k) = \frac{i}{k}\beta P\left[1 - 2\pi n_0 \int_0^\infty g_0(z)\beta\phi'(z)\left(\int_0^z \frac{1-e^{ikz}}{-ikz} z^2\, dz\right) dz\right]^{-1} \tag{7.5}$$

Perhaps the leading distinction is between those profiles that simply decay to the bulk value n_0 and those that decay with oscillation, a distinction that can be made on the basis of the poles of (7.4), i.e., of the zeros of its denominator. Let us set $t = ik$, and write the denominator as

$$\begin{aligned}\mathrm{Den}(t) = 1 &+ 2\pi n_0 \int_0^\infty g_0(z)[-\beta\phi_+'(z)]\left(\int_0^z \frac{e^{zt}-1}{zt} z^2\, dz\right) dz \\ &- 2\pi n_0 \int_0^\infty g_0(z)\beta\phi_-'(z)\left(\int_0^z \frac{e^{zt}-1}{zt} z^2\, dz\right) dz\end{aligned} \tag{7.6}$$

where ϕ has been decomposed into $\phi = \phi_+ + \phi_-$, a repulsive part satisfying $-\beta\phi_+' \geqslant 0$ and an attractive part with $\beta\phi_-' \geqslant 0$. For asymptotic decay of $n_h(z)$ as $e^{-\alpha z}$, Den(t) must have $t = \alpha$ as its root of smallest real part. If ϕ is purely repulsive, $\phi_- = 0$, clearly Den(zt) > 0 for real t, so that only decay with oscillation can occur. If $\phi_- \neq 0$ and the nonvanishing domain of ϕ_- exceeds the finite domain of ϕ_+, which is normally the case, then Den(t) must ultimately go negative, leading to a pure exponential decay component. However, the slowest decay (smallest Re t) can indeed be oscillatory.

For further analysis, a further approximation will be convenient, along the lines of (7.1). We suppose that the interaction ϕ also consists of a hard core blending into a short-range attraction (or repulsion). Then, since $ge^{\beta\phi}$ is continuous together with its first three derivatives, and hence slowly varying, we have

$$g_0(r)\,\nabla\beta\phi(r) = -g_0(r)e^{\beta\phi(r)}\,\nabla e^{-\beta\phi(r)} = -g_a e^{\beta\phi_a}\,\nabla e^{-\beta\phi(r)}$$

for a nominal core diameter a. A typical plot of $g_0 e^{\beta\phi}$ for a high-density Lennard-Jones fluid[3] is shown in Fig. 4. Although the approximate constancy deteriorates away from the core, this is where the multiplier $(e^{-\beta\phi} - 1)'$ has already become small.

[3] Data kindly supplied by M. Rao.

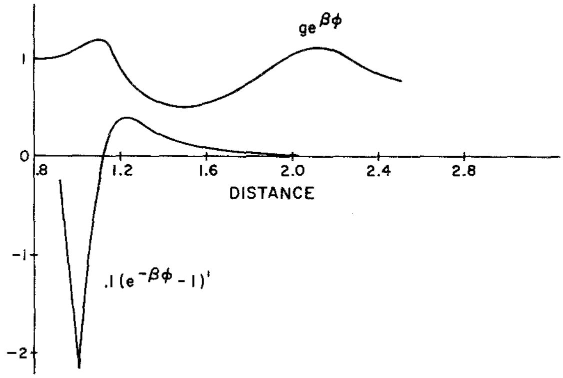

Fig. 4. Plots of $g_e{}^{\beta\phi}$ and $(e^{-1\beta\phi}-1)'$ for uniform Lennard-Jones fluid. $\phi(r)=V(r)-V(r_0)$, with $V(r)=4\epsilon\{[\sigma(r)]^{12}-[\sigma(r)^6]\}$ for $r\leqslant r_0$; $r_0=2.5\sigma$, $n\sigma^3=0.76$, $kT/\epsilon=0.704$; distance in units of σ.

The constant $g_a e^{\beta\phi_a}$ can now be evaluated from the virial pressure:

$$\begin{aligned}\beta P &= n_0\left[1-\tfrac{2}{3}\pi n_0\int_0^\infty g_0(z)\beta\phi'(z)z^3\,dz\right]\\ &\simeq n_0\left[1+\tfrac{2}{3}\pi n_0\int_0^\infty g_a e^{\beta\phi_a}(e^{-\beta\phi(z)}-1)'z^3\,dz\right]\\ &= n_0\left[1-2\pi n_0 g_a e^{\beta\phi_a}\int_0^\infty (e^{-\beta\phi(z)}-1)z^2\,dz\right]\end{aligned}$$

Thus

$$g_a e^{\beta\phi_a}\simeq(\beta P-n_0)/n_0{}^2B_2 \tag{7.7}$$

where

$$B_2=2\pi\int_0^\infty(1-e^{-\beta\phi(z)})z^2\phi z \tag{7.8}$$

is the usual 0-density second virial coefficient. Returning to (7.5), then

$$\begin{aligned}&2\pi n_0\int_0^\infty g_0(z)\beta\phi'(z)\left(\int_0^z\frac{1-e^{ikz}}{-ikz}z^2\,dz\right)dz\\ &\quad\simeq -2\pi n_0 g_a e^{\beta\phi_a}\int_0^\infty(e^{-\beta\phi(z)}-1)'\left(\int_0^z\frac{1-e^{ikz}}{-ikz}z^2\,dz\right)dz\\ &\quad= 2\pi n_0 g_a e^{\beta\phi_a}\int_0^\infty(e^{-\beta\phi(z)}-1)\frac{1-e^{ikz}}{-ikz}z^2\,dz\\ &\quad\simeq\frac{\beta P-n_0}{B_2 n_0}2\pi\int_0^\infty\frac{e^{ikz}-1}{ik}(e^{-\beta\phi(z)}-1)z\,dz\end{aligned}$$

Hence (7.5) becomes

$$\tilde{n}_h(k) = \frac{(i/k)\beta P}{1 + [(\beta P - n_0)/n_0][f(k)/f(0)]} \tag{7.9}$$

where

$$f(k) = 2\pi \int_0^\infty \frac{e^{ikz} - 1}{ik} (1 - e^{-\beta\phi(z)}) z \, dz$$

$$f(0) = B_2 = 2\pi \int_0^\infty (1 - e^{-\beta\phi(z)}) z^2 \, dz$$

An immediate consequence of *this* approximation is that if $n_w = \beta P = n_0$ (but $B_2 \neq 0$), then the profile is perfectly flat: $n(z) = n_0$ for $z > 0$. A comparison (Fig. 5) with numerical simulation experiments (see footnote 3) shows only a small deviation from this rather stringent result.

As with (7.5), the qualitative behavior of the general profile is relatively easy to assess. Again, we go over to $ik = t$:

$$f(-it) = 2\pi \int_0^\infty \frac{e^{tz} - 1}{tz} (1 - e^{-\beta\phi^+(z)}) z^2 \, dz - 2\pi \int_0^\infty \frac{e^{tz} - 1}{tz} (e^{-\beta\phi^-(z)} - 1) z^2 \, dz \tag{7.10}$$

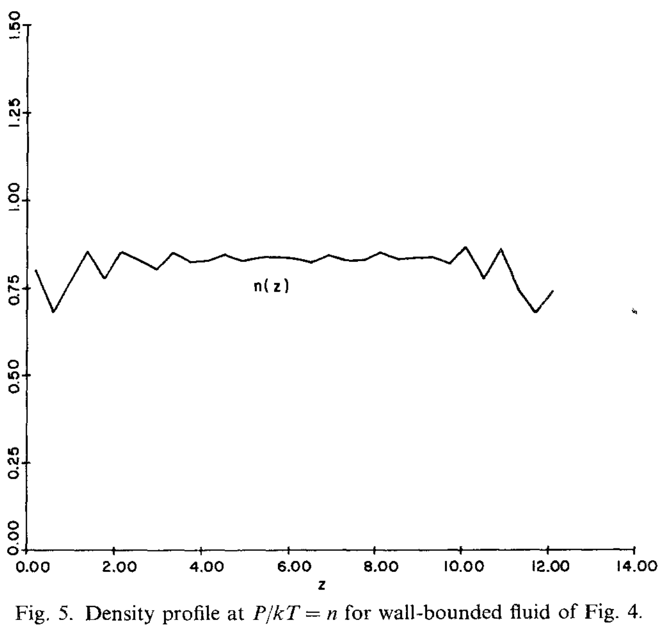

Fig. 5. Density profile at $P/kT = n$ for wall-bounded fluid of Fig. 4.

where now $\phi = \phi^+ + \phi^-$, $\pm\phi^\pm \geqslant 0$. Note first that this definition of $\phi^\pm$ shares the major property of that of (7.6): typically, ϕ^+ exists in a finite domain, followed by the nonvanishing domain of ϕ^-. Thus for any attraction at all, $f(-it)$ ultimately goes negative for large, real t. Since $(\beta P - n_0)/f(0) > 0$, according to (7.7), this signals a pure exponential decay component. At high temperature, where repulsion dominates, we expect the slowest decay to be oscillatory, and it is in principle not difficult to find the temperature at which a real exponent bifurcates into two complex ones: we need both Det $(t) = 0$ and $\partial[\mathrm{Det}(t)]/\partial t = 0$, the latter now reading

$$\int_0^\infty \frac{(1 - tz)e^{tz} - 1}{tz}(1 - e^{-\beta\phi^+(z)})z^2\,dz = \int_0^\infty \frac{(1 - tz)e^{tz} - 1}{tz}(e^{\beta\phi^-(z)} - 1)z^2\,dz \tag{7.11}$$

The local density is not the only useful characterization of a nonuniform fluid. Among the other local quantities that we can define, the local pressure tensor enters prominently into hydrodynamic consequences of nonuniformity. Let us briefly investigate this parameter. We consider the pressure vector or momentum transport across a face Δ^2 of normal $\hat{z}$ centered at $\mathbf{R}$, as indicated in Fig. 6. In the absence of an external potential, this is clearly given by

$$\mathbf{P}_z(\mathbf{R}) = \frac{1}{\beta} n(\mathbf{R})\hat{z} - \frac{1}{\Delta^2} \iint\limits_{\substack{z > Z > z' \\ |x_0 - X| < \Delta/2 \\ |y_0 - Y| < \Delta/2}} n_2(\mathbf{r}, \mathbf{r}')\,\nabla\phi(\mathbf{r} - \mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' \tag{7.12}$$

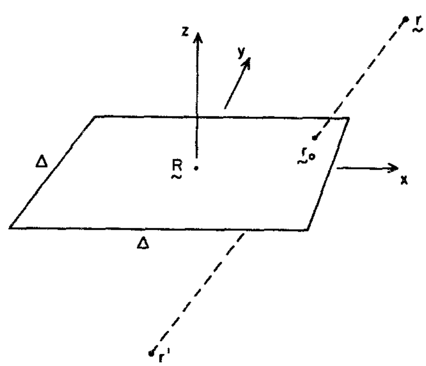

Fig. 6. Geometry of pressure tensor computation.

Since

$$\lim_{\Delta\to 0} (1/\Delta)\epsilon(|x_0 - Xl - \tfrac{1}{2}\Delta) = \delta(x_0 - X)$$

and similarly for y, and we readily find

$$\mathbf{r}_0 = \frac{z - Z}{z - z'}\mathbf{r}' + \frac{Z - z'}{z - z'}\mathbf{r}$$

Eq. (7.12) becomes

$$\mathbf{P}_z(\mathbf{R}) = \frac{1}{\beta} n(\mathbf{R})\hat{z} - \iint n_2(\mathbf{r}, \mathbf{r}')\, \nabla\phi(\mathbf{r}, \mathbf{r}')\epsilon(z - Z)\epsilon(Z - z')$$
$$\times\, \delta\!\left(\frac{z - Z}{z - z'}x' + \frac{Z - z'}{z - z'}x - X\right)\delta\!\left(\frac{z - Z}{z - z'}y' + \frac{Z - z'}{z - z'}y - Y\right) d\mathbf{r}\, d\mathbf{r}' \tag{7.13}$$

Two cases will be of interest for our wall-bounded system with translation invariance in the x–y plane. First is the normal pressure, $\hat{z}$ being the normal direction, for which $\mathbf{P}_N(\mathbf{R})$ is unchanged by averaging over the XY plane of area, say, A:

$$\mathbf{P}_N(Z) = \frac{1}{\beta} n(Z)\hat{z} - \frac{1}{A}\iint n_2(\mathbf{r}, \mathbf{r}')\, \nabla\phi(\mathbf{r} - \mathbf{r}')\epsilon(z - Z)\epsilon(Z - z')\, d\mathbf{r}\, d\mathbf{r}'$$
$$= \frac{1}{\beta} n(Z)\hat{z} - \frac{1}{A}\iint n_2(\mathbf{r}, \mathbf{r}')\, \nabla\phi(\mathbf{r} - \mathbf{r}')\epsilon(Z - z')\, d\mathbf{r}\, d\mathbf{r}' \tag{7.14}$$

(the difference of the integrands is antisymmetric in $\mathbf{r}$ and $\mathbf{r}'$). Since we have tacitly assumed the absence of an external potential, other than the space-limiting wall, in deriving (7.13), the BBGKY equation

$$\nabla n(z')/\beta - \int n_2(\mathbf{r}, \mathbf{r}')\, \nabla\phi(\mathbf{r} - \mathbf{r}')\, d\mathbf{r} = P\, \delta(z')\hat{z}$$

converts this at once to

$$\mathbf{P}_N(Z) = P\hat{z} \tag{7.15}$$

The normal pressure is always equal to the bulk pressure, a fact that we have elaborated upon in Section 4.

The second case is that of the tangential pressure, say across a face with normal $\hat{x}$ in the same physical situation. By cyclic permutation, we replace

(7.13) by

$$\mathbf{P}_x(\mathbf{R}) = \frac{1}{\beta} n(\mathbf{R})\hat{x} - \iint n_2(\mathbf{r}, \mathbf{r}')\, \nabla\phi(\mathbf{r} - \mathbf{r}')\epsilon(x - X)\epsilon(X - x') \times \delta\left(\frac{x - X}{x - x'} y' + \frac{X - x'}{x - x'} y - Y\right) \times \delta\left(\frac{x - X}{x - x'} z' + \frac{X - x'}{x - x'} z - Z\right) d\mathbf{r}\, d\mathbf{r}' \tag{7.16}$$

Integration, over Y and then X, is still easy, and yields

$$\begin{aligned}\mathbf{P}_T(Z) &= \frac{1}{\beta} n(Z)\hat{x} - \frac{1}{A} \iint n_2(\mathbf{r}, \mathbf{r}')\, \nabla\phi(\mathbf{r} - \mathbf{r}') \times \left|\frac{x - X'}{z - z'}\right| \epsilon\left[\frac{x - X'}{z - z'}(z - Z)\right] \epsilon\left(\frac{x - X'}{z - z'}\right) d\mathbf{r}\, d\mathbf{r}' \\ &= \frac{1}{\beta} n(Z)\hat{x} - \frac{1}{A} \iint n_2(\mathbf{r}, \mathbf{r}')\, \nabla\phi(\mathbf{r} - \mathbf{r}') \frac{x - x'}{z - z'} \epsilon(z - Z)\epsilon(Z - z')\, d\mathbf{r}\, d\mathbf{r}' \\ &= \frac{1}{\beta} n(Z)\hat{x} - \frac{1}{A} \iint n_2(\mathbf{r}, \mathbf{r}')\, \nabla\phi(\mathbf{r} - \mathbf{r}') \frac{x - x'}{z - z'} \epsilon(Z - z')\, d\mathbf{r}\, d\mathbf{r}' \end{aligned} \tag{7.17}$$

which is no longer trivial. By x parity, only the x component exists, and this is numerically equal to the y component. Thus we can write

$$P_T(Z) = \frac{1}{\beta} n(Z) - \frac{1}{2A} \iint n_2(\mathbf{r}, \mathbf{r}')\phi'(\mathbf{r} - \mathbf{r}') \times \frac{(x - x')^2 + (y - y')^2}{|\mathbf{r} - \mathbf{r}|(z - z')} \epsilon(Z - z')\, d\mathbf{r}\, d\mathbf{r}' \tag{7.18}$$

A convenient combination to consider is the difference

$$P_T(Z) - P_N(Z) = \frac{1}{2A} \iint n_2(\mathbf{r}, \mathbf{r}')\phi'(\mathbf{r} - \mathbf{r}') \times \frac{2(z - z')^2 - (x - x')^2 - (y - y')^2}{|\mathbf{r} - \mathbf{r}'|(z - z')} \epsilon(Z - z')\, d\mathbf{r}\, d\mathbf{r}' \tag{7.19}$$

which is related to surface tension for a two-phase interface.

Let us now make the shielding approximation:

$$P_T(Z) - P_N(Z) = \frac{n_0}{2A} \iint n(z_<) g_0(\mathbf{r} - \mathbf{r}')\phi'(\mathbf{r} - \mathbf{r}') \times \frac{2(z - z')^2 - (x - x')^2 - (y - y')^2}{|\mathbf{r} - \mathbf{r}'|(z - z')} \epsilon(Z - z')\, d\mathbf{r}\, d\mathbf{r}' \tag{7.20}$$

Integrating first over $\mathbf{x}$ and $\mathbf{x}'$ requires

$$\int_0^\infty f[(\rho^2 + z^2)^{1/2}](2z^2 - \rho^2)2\pi\rho\, d\rho = 2\pi \int_z^\infty f(R)(3z^2 - R^2)R\, dR$$

$$= -2\pi \int_{-z}^\infty f(R)(3z^2 - R^2)R\, dR$$

for odd f, so that (7.20) becomes

$$\Delta P(Z) = \pi n_0 \iint n(z_<) \int_{z-z'}^\infty n g_0(R)\phi'(R) \times \frac{3(z - z') - R^2}{z - z'} dR\, \epsilon(Z - z')\, dz\, dz' \tag{7.21}$$

We can now Fourier transform to yield, for $k \neq 0$,

$$\Delta\tilde{P}(k) = \pi n_0 \tilde{n}(k) \int_0^\infty g_0(R)\phi'(R)\left(\int_0^R \frac{3\zeta^2 - R^2}{\zeta} \frac{e^{ik\zeta} - 1}{ik} d\zeta\right) dR \tag{7.22}$$

which is eminently computable. However, the qualitative nature of ΔP is best appreciated in real space. By reverse Fourier transforming (7.22), we can obtain ΔP in convolution form

$$\Delta P(z) = n(z) * W(z) \tag{7.23}$$

where

$$W(z) = \tfrac{1}{2} n_0 \int_z^\infty g_0(R)\phi'(R)[3(R^2 - z^2) - R^2 \ln R/z]\, dr$$

Or, by expanding (7.22) about $k = 0$,

$$\int_0^\infty g_0(R)\phi'(R) \int_0^R (3\zeta^2 - R^2) \frac{e^{ik\zeta} - 1}{ik\zeta} d\zeta\, dR$$

$$= \frac{1}{4} \int_0^\infty R^4 g_0(R)\phi'(R)\, dR(ik) + \cdots$$

we also have

$$\Delta P(z) = -\left[\tfrac{1}{8}n_0 \int_0^\infty R^4 g_0(R)\phi'(R)\,dR\right] n'(z) + \cdots \qquad (7.24)$$

valid when $n(z)$ is not changing too rapidly.

8. COMPLEX WALL CONFIGURATIONS

8.1. Small Curvature

We proceed now to hard boundaries that are not simply planar or spherical. The general problem is of course more involved than that of a spherical boundary alone, which we did not solve completely even in the context of the shielding approximation. However, we can obtain a quick estimate for a single surface of small local curvature by taking advantage of the spherical case in the small-curvature limit, together with reasonable locality assumptions. For spherical boundary, we have seen [Eqs. (6.14), (6.15)] that, measuring from the surface

$$n_w(r) = n_\infty(r) + \frac{K}{n_0}\left[n_\infty(r) \int_0^\infty x n_\infty'(x)\,dx - n_\infty(\infty) \int_0^r x n_\infty'(x)\,dx\right] \qquad (8.1)$$

where $K = 1/R$ is the curvature of the sphere. For the moment, we leave unspecified the proper generalization of K to a nonspherical surface.

Suppose now that we have a bounding surface whose curvature is small on the scale of the correlation function $g - 1$. To make contact with the locally flat case, it is appropriate to introduce a new coordinate system $\mathbf{R} = (Z, \mathbf{X})$, with $Z = R_0$, $X = R_1$, $Y = R_2$. Here Z is to measure distance to the surface on a trajectory normal to equally spaced surfaces. Thus, the hard wall is defined by

$$Z(\mathbf{r}) \leqslant 0 \qquad (8.2)$$

and we require

$$dZ = dZ(\widehat{\nabla Z}\cdot\nabla)Z \qquad \text{or} \qquad |\nabla Z|^2 = 1 \qquad (8.3)$$

We further define X and Y to be constant along ∇Z:

$$\nabla X\cdot\nabla Z = \nabla Y\cdot\nabla Z = 0 \qquad (8.4)$$

A consequence of (8.3) and (8.4) that we will need later is that

$$\begin{aligned}\partial r_\alpha/\partial Z &= (\partial R/\partial r)^{-1}_{\alpha 0} = \{(\partial R/\partial r)^T[\partial R/\partial r(\partial R/\partial r)^T]^{-1}\}_{\alpha 0}\\ &= \sum (\partial R/\partial r)^T_{\alpha\beta}\,\delta_{\beta 0} = \partial R_0/\partial r_\alpha\end{aligned}$$

or

$$\partial \mathbf{r}/\partial Z = \nabla Z \tag{8.5}$$

Now a surface element $dX\,dY$ continues to a tube measured by Z which is a distorted portion of the conical volume determined by the surface curvature. Thus, we would expect (8.1) to generalize to

$$n_w(\mathbf{R}) = n_\infty(Z) + \frac{K(\mathbf{X})}{n_0} \times \left[n_\infty(Z) \int_0^\infty x n_\infty{}'(x)\,dx - n_\infty(\infty) \int_0^Z x n_\infty(x)\,dx \right] \tag{8.6}$$

whose validity we will now verify. We proceed as follows.

Since the wall potential satisfies

$$e^{-\beta u(\mathbf{r})} = \epsilon(Z(\mathbf{r})) \tag{8.7}$$

the exact first BBGKY equation becomes

$$\nabla n(\mathbf{r}) + \int n_2(\mathbf{r}, \mathbf{r}')\,\nabla\beta\phi(\mathbf{r} - \mathbf{r}')\,dr' = n_w(\mathbf{X}(\mathbf{r}))\,\nabla\epsilon(Z(\mathbf{r})) \tag{8.8}$$

where $n_w(\mathbf{x})$ is the density at the wall location $Z = 0$. We will assess shielding in terms of the Z distance to the wall, so that (8.8) is to be approximated by

$$\nabla n(\mathbf{r}) + n_0 \int [n(\mathbf{r})\epsilon(Z(\mathbf{r}') - Z(\mathbf{r})) + n(\mathbf{r}')\epsilon(Z(\mathbf{r}) - Z(\mathbf{r}'))] \times g_0(\mathbf{r} - \mathbf{r}')\,\nabla\beta\phi(\mathbf{r} - \mathbf{r}')\,d\mathbf{r}' = n_w(X(\mathbf{r}))\,\nabla\epsilon(Z(\mathbf{r})) \tag{8.9}$$

simplifying to

$$\nabla n(\mathbf{r}) + n_0 \int [n(\mathbf{r}') - n(\mathbf{r})]\epsilon(Z(\mathbf{r}) - Z(\mathbf{r}')) \times g_0(\mathbf{r} - \mathbf{r}')\,\nabla\beta\phi(\mathbf{r} - \mathbf{r}')\,d\mathbf{r}' = n_w(X(\mathbf{r}))\,\nabla\epsilon(Z(\mathbf{r}')) \tag{8.10}$$

If we measure density as well in the new coordinate system,

$$n(\mathbf{r}) = n_w(\mathbf{R}(\mathbf{r}')) \tag{8.11}$$

then with ∇ denoting $\partial/\partial\mathbf{R}$, (8.10) can be written as well as

$$\nabla n_w(\mathbf{R}) + n_0 \int [n_w(\mathbf{R}') - n_w(\mathbf{R})]\epsilon(Z - Z') \times g_0(\mathbf{r} - \mathbf{r}')\,\nabla\beta\phi(\mathbf{r} - \mathbf{r}')\,d\mathbf{r}' = n_w(\mathbf{X})\,\nabla\epsilon(Z) \tag{8.12}$$

But since (8.12) is already an approximation, a consistency problem must be noted: Eq. (8.12) is a three-vector equation for the scalar $n_w(\mathbf{R})$ and its restriction

$$n_w(\mathbf{X}) = n_w(0, \mathbf{X}) \tag{8.13}$$

and hence need not be soluble. To avoid this difficulty, we shall consider only the Z component,

$$\frac{\partial}{\partial Z} n_w(\mathbf{R}) + n_0 \int [n_w(\mathbf{R}') - n_w(\mathbf{R})] \epsilon(Z - Z') \times g_0(\mathbf{r} - \mathbf{r}') \frac{\partial}{\partial Z} \beta\phi(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}' = n_w(\mathbf{X})\, \delta(Z) \tag{8.14}$$

which is all that would exist for the planar wall case.

For analytic tractability, we now introduce the small-curvature assumption in a fashion suggested by the case of a spherical boundary of radius a. In the latter spherical case, with $a + R$, θ, ϕ measured from the center of the sphere, the approximate transformation can be written as

$$\begin{aligned} z/a &= (1 + R/a)\cos\theta - 1 \\ x/a &= (1 + R/a)\sin\theta\cos\phi \\ y/a &= (1 + R/a)\sin\theta\sin\phi \end{aligned} \tag{8.15}$$

and indeed R is the physical distance to the surface along its own gradient. In general, then, we imagine X and Y to be angular coordinates, and so set

$$\mathbf{r} = (1/\gamma)\mathbf{\Lambda}(\gamma Z, \mathbf{X}) \tag{8.16}$$

where $\mathbf{\Lambda}(\mathbf{0}) = \mathbf{0}$, the limit $\gamma \to 0$ then corresponding to indefinite expansion of the surface and its equidistant neighbors about the origin, the conditions (8.3) and (8.4), however, being maintained in the process.

We must now set up (8.14) to be suitable for taking the limit of small γ. To this end, we observe that $|\mathbf{r} - \mathbf{r}'|$ in the integrand of (8.14) is bounded for short-range ϕ, and hence from (8.16), $|\mathbf{x} - \mathbf{x}'| \to 0$ as $\gamma \to 0$. Thus we will eliminate the primed variables by defining

$$\mathcal{R} - \mathcal{R}' = \gamma\xi, \qquad \mathcal{R} = (\gamma Z, \mathbf{X}) \tag{8.17}$$

and setting

$$\eta = \mathbf{r} - \mathbf{r}' \tag{8.18}$$

Since $\phi(\mathbf{r} - \mathbf{r}') = \phi(|\mathbf{r} - \mathbf{r}'|)$, (8.14) becomes in obvious notation

$$\frac{\partial \mathcal{R}}{\partial Z} n_w(Z, \mathbf{X}) + n_0 \int [n_w(Z - \xi_0, \mathbf{X} - \gamma\xi) - n_w(z, \mathbf{X})] \epsilon(\xi_0) \times g_0(\eta) \sum \eta_\alpha \frac{\partial \Lambda_\alpha}{\partial \mathcal{R}_0} \frac{1}{\eta} \beta\phi'(\eta)\, d^3\eta = n_w(\mathbf{X})\, \delta(Z) \tag{8.19}$$

Expanding $r - r'$ in α, we have

$$\eta_\alpha = \sum \frac{\partial \Lambda_\alpha}{\partial \mathscr{R}_0} \xi_\mu - \frac{\gamma}{2} \sum \frac{\partial^2 \Lambda_\alpha}{\partial \mathscr{R}_\mu \, \partial \mathscr{R}_\nu} \xi_\mu \xi_\nu + \cdots \tag{8.20}$$

together with its inverse

$$\xi_\alpha = \sum \frac{\partial \mathscr{R}_\alpha}{\partial \Lambda_\mu} \eta_\mu - \frac{\gamma}{2} \sum \frac{\partial^2 \mathscr{R}_\alpha}{\partial \Lambda_\mu \, \partial \Lambda_\nu} \eta_\mu \eta_\nu + \cdots \tag{8.21}$$

Since $|\nabla Z|^2 = \sum (\partial \mathscr{R}_0 / \partial \Lambda_\alpha)^2 = 1$, then

$$\eta_z = \sum \frac{\partial \mathscr{R}_0}{\partial \Lambda_\mu} \eta_\mu \tag{8.22}$$

in the component ∇Z of η, as in $\sum (\partial \Lambda_\alpha / \partial \mathscr{R}_0) \eta_\alpha$, according to (8.5). Thus to first order in γ,

$$\begin{aligned} &\frac{\partial}{\partial Z} n_w(Z, X) + n_0 \int n_w\left(Z - \eta_z + \frac{\gamma}{2} \sum \frac{\partial^2 \mathscr{R}_0}{\partial \Lambda_\mu \, \partial \Lambda_\nu} \eta_\mu \eta_\nu, X \right. \\ &\quad \left. - \gamma \sum \frac{\partial X}{\partial \Lambda_\mu} \eta_\mu - n_w(Z, X)\right) \epsilon\left(\eta_z - \frac{\gamma}{2} \sum \frac{\partial^2 \mathscr{R}_0}{\partial \Lambda_\mu \, \partial \Lambda_\nu} \eta_\mu \eta_\nu\right) \eta_z g_0(\eta) \frac{1}{\eta} \\ &\quad \times \phi(\eta) \, d^3\eta = n_w(\mathbf{X}) \, \delta(Z) \end{aligned} \tag{8.23}$$

or, expanding further,

$$\begin{aligned} &\frac{\partial}{\partial Z} n_w(Z, \mathbf{X}) + n_0 \int [n_w(Z - \eta_z, X) - n_w(Z, X)] \epsilon(\eta_z) \eta_z g_0(\eta) \frac{1}{\eta} \phi'(\eta) \, d^3\eta \\ &\quad + \gamma n_0 \int \left(\left(\frac{1}{2} \sum \frac{\partial^2 \mathscr{R}_0}{\partial \Lambda_\mu \, \partial \Lambda_\nu} \eta_\mu \eta_\nu \frac{\partial}{\partial Z} - \sum \frac{\partial \mathbf{X}}{\partial \Lambda_\mu} \eta_\mu \cdot \nabla \right) n_w(Z - \eta_z, \mathbf{X}) \right) \\ &\quad \times \epsilon(\eta_z) \eta_z g_0(\eta) \frac{1}{\eta} \phi'(\eta) \, d^3\eta = n_w(\mathbf{X}) \, \delta(Z) \end{aligned} \tag{8.24}$$

where all partial derivatives are to be evaluated at $\mathscr{R}_0 = \gamma Z = 0$.

The correction term in (8.24) has bilinear and trilinear contributions in the η_α. By η parity perpendicular to ∇Z, the bilinear terms require consideration only of $(\partial \mathbf{X}/\partial \Lambda_\mu)_z = (\partial \mathbf{X}/\partial \Lambda_\mu) \, \partial \Lambda_\mu / \partial \mathscr{R}_0 = 0$ and hence do not appear. Similarly, for the trilinear terms, we need only $\partial^2 \mathscr{R}_0 / \partial \Lambda_\alpha{}^2$ for $\alpha = z$ or $\alpha = p, q$ perpendicular to ∇Z. But

$$\partial^2 \mathscr{R}_0 / \partial \Lambda_z{}^2 = \sum (\partial^2 \mathscr{R}_0 / \partial \Lambda_\mu \, \partial \Lambda_\nu)(\partial \mathscr{R}_0 / \partial \Lambda_\mu) \, \partial \Lambda_\nu / \partial \mathscr{R}_0 = 0$$

$$\frac{1}{2} \sum (\partial \Lambda_\nu / \partial \mathscr{R}_0)(\partial / \partial \Lambda_\nu)(\partial \mathscr{R}_0 / \partial \Lambda_\mu)^2 = 0$$

since $|\nabla Z|^2 = 1$. Of course $\alpha_p{}^2$ and $\alpha_q{}^2$ give equal contributions, and so $\sum (\partial^2\mathscr{R}_0/\partial\Lambda_\mu\,\partial\Lambda_\nu)\eta_\mu\eta_\nu(\partial^2\mathscr{R}_0/\partial\Lambda_p{}^2 + \partial^2\mathscr{R}_0/\partial\Lambda_q{}^2)\eta_p{}^2 = (1/\gamma^2)\,\nabla_0{}^2\tfrac{1}{2}(\eta^2 - \eta_z{}^2)$ yielding the further simplification

$$\frac{\partial}{\partial Z} n_w(Z, \mathbf{X}) + n_0[n_w(Z - n_z, X) - n_w(Z, \mathbf{X})]\epsilon(\eta_Z)\eta_z g_0(\eta)\frac{1}{\eta}\beta\phi'(\eta)\,d^3\eta$$
$$+ \frac{n_0}{2}(\nabla^2 Z)_0 \frac{\partial}{\partial Z}\int n_w(z - \eta_z, \mathbf{X})\epsilon(\eta_Z)\tfrac{1}{2}\eta_z(\eta^2 - \eta_z{}^2)g_0(\eta)\frac{1}{\eta}$$
$$\times\, \phi'(\eta)\,d^3\eta = n_w(\mathbf{X})\,\delta(Z) \tag{8.25}$$

Equation (8.25) can be solved by one-dimensional Fourier transform:

$$\left[-ik + n_0\int\epsilon(z)(e^{ikz} - 1)g_0(r)\frac{z}{r}\beta\phi'(r)\,d^3r - \frac{n_0}{2}(\nabla^2 Z)_0 ik\int\epsilon(z)e^{ikz}g_0(r)\right.$$
$$\left.\times\frac{1}{2}\frac{z}{r}(r^2 - z^2)\beta\phi'(r)\,d^3r\right]\tilde{n}_w(k, \mathbf{X}) = n_w(\mathbf{X}) \tag{8.26}$$

This is further reduced by inserting $\tilde{n}_\infty(k)$ of (5.5) and observing that since

$$\int g_0(r)\frac{z}{r}\beta\phi'(r)f(z)\,d^3r = 2\pi\int_0^\infty g_0(r)\beta\phi'(r)\left[\int_0^r zf(z)\,dZ\right]dr \tag{8.27}$$

while

$$\int_0^r (r^2 - z^2)ze^{ikz}\,dZ = 2\left(\frac{1}{ik}\frac{\partial}{\partial ik} - \frac{1}{(ik)^2}\right)\int_0^r z(e^{ikz} - 1)\,dz \tag{8.28}$$

it follows that

$$n_0\int\epsilon(z)\tfrac{1}{2}(r^2 - z^2)e^{ikz}g_0(r)\frac{z}{r}\beta\phi'(r)\,d^3r$$
$$= \left[\frac{1}{ik}\frac{\partial}{\partial ik} - \frac{1}{(ik)^2}\right]\left[-ik + n_0\int\epsilon(z)(e^{ikz} - 1)g_0(r)\frac{z}{r}\beta\phi'(r)\,d^3r\right]$$
$$= \frac{1}{ik}\left(\frac{\partial}{\partial ik} - \frac{1}{ik}\right)\frac{\beta P}{\tilde{n}_\infty(k)} \tag{8.29}$$

Hence (8.26) can be written as

$$\left[\frac{\beta P}{\tilde{n}_\infty(k)} - \tfrac{1}{2}(\nabla^2 Z)_0\left(\frac{\partial}{\partial ik} - \frac{1}{ik}\right)\frac{\beta P}{\tilde{n}_\infty(k)}\right]\tilde{n}_w(k, \mathbf{X}) = \tilde{n}_w(\mathbf{X}) \tag{8.30}$$

and solved to first order in $(\nabla^2 Z)_0$ as

$$\tilde{n}_w(k, \mathbf{X}) = \left[\frac{n_w(\mathbf{X})}{\beta P} - \tfrac{1}{2}(\nabla^2 Z)_0\left(\frac{\partial}{\partial ik} + \frac{1}{ik}\right)\right]\tilde{n}_\infty(k) \tag{8.31}$$

Reverse Fourier transforming,

$$n_w(Z, \mathbf{X}) = \frac{n_w(\mathbf{X})}{\beta P} n_\infty(Z) - \tfrac{1}{2}(\nabla^2 Z)_0 \int_0^z z n_\infty'(Z)\, dZ \tag{8.32}$$

and, since $n_w(\infty, \mathbf{X}) = n_0$, then

$$n_w(\mathbf{X}) = \beta P\left[1 + \frac{1}{2}\frac{(\nabla^2 Z)_0}{n_0}\int_0^\infty z n_\infty'(z)\, dZ\right] \tag{8.33}$$

yielding the final expression

$$\begin{aligned} n_w(z, \mathbf{X}) = n_\infty(Z) &+ \frac{1}{2}\frac{(\nabla^2 Z)_0}{n_0} \\ &\times \left[n_\infty(Z)\int_0^\infty z n_\infty'(z)\, dz - n_\infty(\infty)\int_0^Z z n_\infty'(z)\, dz\right] \end{aligned} \tag{8.34}$$

We conclude that the educated guess (8.6) is indeed correct to first order in the curvature, and that the relevant curvature is

$$K(\mathbf{X}) = \tfrac{1}{2}(\nabla^2 Z)_{Z=0} \tag{8.35}$$

8.2. Multiple Surfaces

There is another generalization, which makes contact with recent experimental work,[18] and which can be analyzed completely in the context of the shielding approximation. It is that in which the wall consists of two or more separate boundaries. Consider two walls w_1 and w_2 and a designation of particle ordering such that if particle 1 is closer to w_1 than particle 2, then it is automatically further from the wall w_2 (Fig. 7). Let us then examine the pair distribution $n_2(1, 2|w_1 w_2)$. Applying the shielding ansatz twice, we have

$$\begin{aligned} n_2(1, 2|w_1, w_2) &= n_2(1|2, w_1, w_2)n(2|w_1, w_2) \approx n_2(1|2, w_1)n(2|w_1, w_2) \\ &= \frac{n_2(1, 2|w_1)}{n(2|w_1)} n(2|w_1, w_2) = \frac{n(2|1, w_1)n(1|w_1)}{n(2|w_1)} n(2|w_1, w_2) \\ &\approx \frac{n(2|1)n(1|w_1)}{n(2|w_1)} n(2|w_1, w_2) \end{aligned}$$

or

$$n_2(1, 2|w_1, w_2) \approx \frac{n_2(1, 2)}{n(1)}\frac{n(1|w_1)}{n(2|w_1)} n(2|w_1, w_2) \tag{8.36}$$

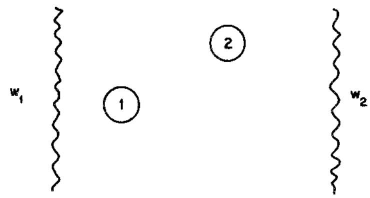

Fig. 7. Shielding configuration for two walls.

On the other hand, reversing the roles of 1 and 2, we also have

$$n_2(1, 2|w_1, w_2) \approx \frac{n_2(1, 2)}{n(2)} \frac{n(2|w_2)}{n(1|w_2)} n(1|w_1, w_2) \tag{8.37}$$

Equations (8.36) and (8.37) are consistent if

$$n(2|w_1, w_2)n(2)/n(2|w_1)n(2|w_2) = n(1|w_1, w_2)n(1)/n(1|w_1)n(1|w_2)$$

and hence if

$$n(1|w_1, w_2) = C[n(1|w_1)n(1|w_2)/n(1)] \tag{8.38}$$

for a suitable contact C. Under these circumstances, (8.36) and (8.37) reduce to

$$n_2(1, 2|w_1, w_2) = C\frac{n_2(1, 2)}{n(1)n(2)} n(1|w_1)n(2|w_2) \tag{8.39}$$

where, it must be emphasized, particle 1 is closer to w_1, particle 2 to w_2.

Suppose there is no external field other than the walls. If the walls are separated sufficiently from any point $\mathbf{r}_1$ that the fluid is guaranteed uniform at $\mathbf{r}_1$, evaluation of (8.36) yields $C = 1$, so that

$$n(1|w_1, w_2) = n(1|w_1)n(2|w_2)/n_0 \tag{8.40}$$

Equation (8.40) is a generalized superposition principle: if w_1 and w_2 represent other particles at, say points 2 and 3, it becomes

$$n_3(1, 2, 3)/n_2(2, 3) = n_2(1, 2)n_2(1, 3)/n_0^3$$

the usual Kirkwood superposition. Equation (8.39), on the other hand, yields

$$n_4(1, 2, 3, 4)/n_2(3, 4) = n_2(1, 2)n_2(1, 3)n_2(2, 4)/n_0^4$$

where 1 is closer to 3 than to 4, and 2 closer to 4, a modified superposition principle.

To the extent that (8.40) is valid, it offers an immediate solution to multi-boundary problems. For example, consider the force between parallel planes of separation z immersed in a fluid of bulk density n_0, pressure P (Fig. 8). The force is proportional to the wall pressure and hence to the wall density.

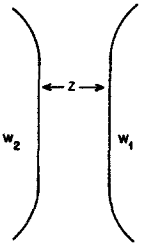

Fig. 8. Wall geometry for Eq. (8.41).

According to (8.40), taking particle 1 at the wall w_1 (recalling that the wall location is defined by its exclusion of particle *centers*), we have[4]

$$n(w_1|w_1, w_2) = (\beta P/n_0)n(z|w_2) \tag{8.41}$$

In the experiments alluded to, a stack of separated lamellae is monitored for intersurface distance as a function of the bulk pressure of surrounding water. The spacing is determined by the outer (two) lamellae, which must balance external pressure P with the force $n(w)/\beta$ due to the fluid extending to the next lamellar surface, and the van der Waals attraction $-P(z)$ between it and its neighbor. Thus, $P = n(w_1|w_1, w_2)/\beta - P(z)$, so that to the extent that water can be regarded as a simple fluid, Eq. (8.41) implies

$$P(z) = P[n(z|w_2) - n_0]/n_0 \tag{8.42}$$

What we can do quite easily is see how experimental observation might be used to obtain the short-range surface–surface van der Waals interaction. Consider, for example, the high-pressure region, in which case we are interested in low z. Now for z less than core diameter σ [$\phi(z) \approx 0$ for $z < \sigma$], (5.3) becomes

$$\frac{\partial n(z)}{\partial z} + \kappa n(z) = \beta P\, \delta(z) + \kappa' \int_0^z \int_0^{z'} n(z'')\, dz''\, dz' \tag{8.43}$$

where

$$\kappa = -\pi n_0 \int_0^\infty R^2 g_0(R)\beta\phi'(R)\, dR, \qquad \kappa' = -2\pi n_0 \int_0^\infty g_0(R)\beta\phi'(R)\, dr$$

which one can compare with

$$3(\beta P - n_0)/n_0 = -2\pi n_0 \int_0^\infty R^3 g_0(R)\beta\phi'(R)\, dR$$

[4] See Ref. 19 for an alternative formalism.

by writing

$$\kappa = (3/2n_0 a)(\beta P - n_0), \qquad \kappa' = (3/n_0 a'^3)(\beta P - n_0) \tag{8.44}$$

a and a' being of the order of the core size.

Equation (8.43), as a linear differential equation in

$$\int_0^z \int_0^{z'} n(z'')\, dz''\, dz'$$

solves as a sum of three exponentials. For large $\beta P/n_0$, and hence large κ and κ', one readily finds

$$n(z) = \beta P\{e^{-\kappa z} + (\kappa'/\kappa^3)^{1/2} \sinh[(k'/k)z]\} \tag{8.45}$$

which is to be inserted into (8.42). On the other hand, for large P, since $P(z)$ will certainly not rise as rapidly as P, the lamellar spacing should be determined simply by $n(z) = n_0$, or $z = \kappa^{-1} \ln(\beta P/n_0)$:

$$z \simeq \tfrac{2}{3} a \frac{\ln(\beta P/n_0)}{\beta P/n_0} \tag{8.46}$$

This region has not yet been attained.

9. CORRECTION SEQUENCES

The shielding approximation is of course just a first step. It is best, but hardly perfect, for describing normal correlations and surely inadequate for describing transverse correlations. There are a number of techniques that can be used to improve the accuracy of these incompletely shielded correlations, and we will now discuss a few of these, mainly in the context of the pair distribution.

The ansatz (2.4), as we have noted, is clearly unsuitable for large separation, where we should have $n_2(\mathbf{r}, \mathbf{r}') \to n(\mathbf{r})n(\mathbf{r}')$. One way of stating this is in the form

$$n(2|1, w) = \sigma(2|1, w)n(2|1) + [1 - \sigma(2|1, w)]n(2|w) \tag{9.1}$$

where $z_1 < z_2$. Here the "shadow function" $\sigma \sim 1$ when particle 1 blocks particle 2's view of the wall, but $\sigma \sim 0$ when particle 1 is out of the way. We further know from an analysis of long-range transverse correlations that in its decaying phase, σ has the form

$$\sigma(2|1, w) \sim a(z_1, z_2)K_0(\alpha|\mathbf{x}_1 - \mathbf{x}_2|) \tag{9.2}$$

when the primary mechanism for transverse correlations is the excitation and quenching of capillary waves.

While the direct physical significance of (9.2) recommends it as the basis of a correction procedure, this has yet to be carried out. The more formal technique of using higher order members of the BBGKY hierarchy to correct the earlier equations is, however, quite easy to introduce, and so we turn instead to the topic. We again base our analysis on the fundamental

$$\nabla_1 n(1) + n(1)\,\nabla\beta u(1) + \int n_2(1,2)\,\nabla_1\beta\phi(1,2)\,d2 = 0 \tag{9.3}$$

but instead of inserting some inspired guess for n_2, we introduce n_2 via the next equation,

$$\begin{aligned}\nabla_1 n_2(1,2) + n_2(1,2)[\nabla_1\beta u(1) + \nabla_1\beta\phi(1,2)]\\ + \int n_3(1,2,3)\,\nabla_1\beta\phi(1,3)\,d3 = 0\end{aligned} \tag{9.4}$$

or via its symmetrized version

$$\begin{aligned}(\nabla_1 + \nabla_2)n_2(1,2) + n_2(1,2)(\nabla_1 + \nabla_2)[\beta u(1) + \beta u(2)]\\ + \int n_3(1,2,3)(\nabla_1 + \nabla_2)[\beta\phi(1,3) + \beta\phi(2,3)]\,d3 = 0\end{aligned} \tag{9.5}$$

and confine our inspired guesswork to n_3, whose effect upon n_2 is now once removed.

As a trivial example suppose that we were to approximate $n_2(1,2)$ by its bulk system value $n_{20}(1,2)$. Since, for a uniform system,

$$\int n_{20}(1,2)\,\nabla_1\beta\phi(1,2)\,d2 = -\nabla_1 n_0 = 0$$

(9.3) reduces to

$$\nabla_1 n(1) + n(1)\,\nabla\beta u(1) = 0 \tag{9.6}$$

so that

$$n(1) = n_0 e^{-\beta u(1)} \tag{9.7}$$

which for a hard-wall potential would cause the density to simply drop from its bulk value of n_0 to 0 at the wall. But suppose instead that we approximate $n_3(1,2,3)$ in (9.5) by its bulk value $n_{30}(1,2,3)$. Since

$$\int n_{30}(1,2,3)[\nabla_1\beta\phi(1,3) + \nabla_2\beta\phi(2,3)]\,d3 = -(\nabla_1 + \nabla_2)n_{20}(1,2) = 0$$

(9.4) then yields

$$(\nabla_1 + \nabla_2)n_2(1,2) + n_2(1,2)[\nabla\beta u(1) + \nabla\beta u(2)] = 0 \tag{9.8}$$

with the solution

$$n_2(1, 2) = n_{20}(1, 2)e^{-\beta[u(1)+u(2)]} \tag{9.9}$$

Now inserting (9.9) into (9.3), we have

$$\nabla_1[n(1)e^{\beta u(1)}] + \int n_{20}(1, 2)e^{-\beta u(2)}\, \nabla_1 \beta\phi(1, 2)\, d2 = 0 \tag{9.10}$$

If u represents a wall to the left of $z = 0$, then (9.9) simply cuts off $n_2(1, 2)$ at the wall, and (9.10) integrates to

$$\begin{aligned} n(1)e^{\beta u(1)} &= n_0 + n_0^2 \int_{z_1}^{\infty} \int_0^{\infty} \int g_0(1-2) \frac{\partial}{\partial z_1} \beta\phi(1-2)\, d^2x_2\, dz_2\, dz_1 \\ &= n_0 - 2\pi n_0^2 \int_{z_1}^{\infty} (\tfrac{1}{3}R^3 - \tfrac{1}{2}z_1 R^2 + \tfrac{1}{6}z_1^3) g(R) \beta\phi'(R)\, dR \end{aligned} \tag{9.11}$$

which has a reasonable initial decay from the correct n_w but no further oscillational structure.

To improve the inserted function n_3, we now use the shielding approximation that was reasonably effective for n_2. As we have seen in Section 2, there are strong and weak versions of shielding, depending upon whether one particle shields the other two from the wall, or a pair of particles shields the third. In the first case, according to (2.17),

$$n_3(1, 2, 3|w) = [n(r_<|w)/n_0] n_{30}(1, 2, 3) \tag{9.12}$$

where $r_<$ denotes the closest of particles 1, 2, 3, so that (9.5) becomes

$$\begin{aligned} &(\nabla_1 + \nabla_2) n_2(1, 2) + n_2(1, 2)(\nabla_1 + \nabla_2)[\beta u(1) + \beta u(2)] \\ &\quad + (1/n_0) \int n_{30}(1, 2, 3) n(r_<) \\ &\quad \times (\nabla_1 + \nabla_2)[\beta\phi(1, 3) + \beta\phi(2, 3)]\, d3 = 0 \end{aligned} \tag{9.13}$$

Again using the bulk information

$$\int n_{30}(1, 2, 3)(\nabla_1 + \nabla_2)[\beta\phi(1, 3) + \beta\phi(2, 3)]\, d3 = 0$$

we can write (9.13) as

$$\begin{aligned} &(\nabla_1 + \nabla_2) n_2(1, 2) + n_2(1, 2)(\nabla_1 + \nabla_2)[\beta u(1) + \beta u(2)] \\ &\quad + (1/n_0) \int n_{30}(1, 2, 3)[n(r_<) - n(r_{\min})] \\ &\quad \times (\nabla_1 + \nabla_2)[\beta\phi(1, 3) + \beta\phi(2, 3)]\, d3 = 0 \end{aligned} \tag{9.14}$$

where $r_{\min}$ is the nearest of particles 1 and 2, and then as

$$\left(\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right)\frac{n_2(1,2)}{n_0{}^2 g_0(1,2)}+\frac{n_2(1,2)}{n_0{}^2 g_0(1,2)}\left(\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right)[\beta u(1)+\beta u(2)]$$
$$= n_0\iint^{z_{\min}}\frac{g_{30}(1,2,3)}{ng_0(1,2)}[n(z_3)-n(z_{\min})]\frac{\partial}{\partial z_3}$$
$$\times[\beta\phi(1,3)+\beta\phi(2,3)]\,dz_3\,d^2x_3 \tag{9.15}$$

where $g_{30}=n_{30}/n_0{}^3$. If u represents a hard wall at $z=0$, (9.15) yields after a little algebra

$$\frac{n_2(1,2)}{n_0{}^2 g_0(1,2)}=1+n_0\iint^{z_{\min}}\frac{g_{30}(1,2,3)}{g_0(1,2)}\int_{z_3}^{z_{\min}}[n(z)-n_0]\,dz\frac{\partial}{\partial z_3}$$
$$\times[\beta\phi(1,3)+\beta\phi(2,3)]\,dz_3\,d^2x_3 \tag{9.16}$$

for $z_1, z_2 \geqslant 0$. The consequences of the presumably superior approximation (9.16) are now under investigation.

In the weak version of shielding, (9.12) is replaced by (2.16):

$$n_3(1,2,3|w)=n_{30}(1,2,3)[n_2(r_<,r_M|w)/n_{20}(r_<,r_M)] \tag{9.17}$$

Equation (9.5) yields

$$(\nabla_1+\nabla_2)\frac{n_2(1,2)}{n_{20}(1,2)}+\frac{n_2(1,2)}{n_{20}(1,2)}(\nabla_1+\nabla_2)[\beta u(1)+\beta u(2)]$$
$$=\frac{n_{30}(1,2,3)}{n_{20}(1,2)}\int\frac{n_2(r,r_M)}{n_{20}(r,r_M)}\nabla_3[\beta\phi(1,3)+\beta\phi(2,3)]\,d3 \tag{9.18}$$

which is readily transformed to

$$\left(\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right)\frac{n_2(1,2)}{n_{20}(1,2)}+\frac{n_2(1,2)}{n_{20}(1,2)}\left(\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right)[\beta u(1)+\beta u(2)]$$
$$=\int_{z_3<z_{\max}}\frac{n_{30}(1,2,3)}{n_{20}(1,2)}\left(\frac{n_2(r_{\min},r_3)}{n_{20}(r_{\min},r_3}-\frac{n_2(r_1,r_2)}{n_{20}(r_1,r_2)}\right)\frac{\partial}{\partial z_3}$$
$$\times[\beta\phi(1,3)+\beta\phi(2,3)]\,d3 \tag{9.19}$$

Thus we have created a self-contained approximation for $n_2(1,2)/n_{20}(1,2)$ whose analytic solvability depends very much on the form of n_{30} that is chosen. Although the resulting n_2 need not be highly accurate, e.g., for transverse correlations, its substitution into (9.3) should result in a considerable improvement for the profile $n(1)$.

10. CONCLUSION

We have examined classical fluids primarily in the presence of planar boundaries. The fact that a particle in a one-dimensional system of particles with cores is shielded from direct action of the boundary by intervening particles has a natural extension to two- or three-dimensional fluids. If attention is restricted to lower order distribution functions, only a few particles are available to provide guaranteed shielding, and the approximation fails as soon as these particles are too far away. Thus, a formulation is required in which one never considers widely separated particles, and this is accomplished by the BBGKY hierarchy when the interaction is of short range. Using only one-body shielding, quite satisfying results are obtained in the prototype case of a hard-core fluid, and it seems not too difficult to further improve the technique by considering, implicitly or explicitly, large sets of shielding particles.

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