Journal of Statistical Physics, Vol. 52, Nos. 5/6, 1988

Free Energy Models for Nonuniform Classical Fluids

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Received March 16, 1988

A number of techniques are presented for extrapolating from knowledge of the direct correlation function for a uniform fluid at various densities to that of the free energy and associated density profile of a nonuniform fluid. A primitive mathematical model is followed by models based upon physical characteristics of exactly solved systems, from the nonnegativity of linear response functions to the explicit form of a nonuniform hard rod fluid. Attention is paid to physical requirements which are not satisfied and suggestions are made for future progress.

KEY WORDS: Nonuniform fluid; density functional; profile equation; positivity restrictions.

1. INTRODUCTION

The theoretical analysis of nonuniform classical fluids in thermal equilibrium is a very old topic indeed. One can go back to Archimedes, who presumably knew—in his own terms—that a volume τ of single-component simple fluid subjected to a macroscopic force field $F(r)$ balanced this force against the pressure forces exerted on its surface $\partial\tau$, i.e.,

$$\int_{\tau} F(r)\, n(r)\, d^3r = \int_{\partial\tau} P(n(r))\, dS \tag{1.1}$$

where $P(n)$ denotes the equation of state, $n(r)$ the fluid density, and dS the outwardly directed surface element. Consequently, letting $\tau \to 0$, one has

$$F(r)\, n(r) = \nabla P(n(r)) \tag{1.2}$$

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0022-4715/88/0900-1157$06.00/0

If the force is derived from a potential $F = -\nabla u$, one then has

$$\frac{1}{n(1)} \nabla P(n(r)) + \nabla u(r) = 0 \tag{1.3}$$

or, by virtue of the thermodynamic relation $dP = n\, d\mu$, where μ is the chemical potential, $\nabla(\mu(n(r)) + u(r)) = 0$, integrating to

$$\mu - u(r) = \mu(n(r)) \tag{1.4}$$

for appropriate constant μ. This, in modern terms, is the *profile equation* for a slowly varying external field.

Although (1.4) is perfectly satisfactory$^{(1)}$ for a fluid whose density changes slowly in response to the external field, it is clearly inadequate at a wall or at a two-phase interface, where the density changes on a microscopic scale. In such cases, the density change is not negligible within the correlation length that defines the minimum distance over which a fluid has to be uniform in order that its bulk properties be applicable. When this situation confronted van der Waals two millenia later, his solution$^{(2)}$ (after false starts by such luminaries as Rayleigh$^{(3)}$) was, in essence, to imagine the intermolecular interaction divided into a small primitive core whose associated fluid has a small correlation length and a longer range tail potential $-\phi_1(r - r')$ (without which a two-phase separation could not occur). Under these circumstances, a core particle would be immersed in both the external potential field $u(r)$ and an "internal" average field due to the other core particles

$$\phi_{\text{int}}(r) = -\int \phi_1(r - r')\, n(r')\, d^3r' \tag{1.5}$$

so that (1.4) becomes instead

$$\mu - u(r) = \mu_0(n(r)) - \int \phi_1(r - r')\, n(r')\, d^3r' \tag{1.6}$$

Here, $\mu_0(n)$ expresses the thermodynamics of the core fluid.

The van der Waals approach, useful well beyond the range of its assumption, does have two obvious deficiencies: the core-fluid correlation length is not negligible on the scale of the tail potential, so that short-range fluctuational effects, e.g., at a boundary, are poorly estimated, and the mean field evaluation of the effective potential omits its rather substantial fluctuations. Of course, neither criterion is damning (although the mean field technique makes confusing predictions (see, e.g., ref. 4) as to the capillarly waves that ride on an interfacial surface), since it may be that effective parameters fitted to one type of observation will do quite well on other types. But something more controllable, more of a first-principles approach, would clearly be preferable. Unfortunately, this is not only a difficult task, but one which runs the risk of providing a formulation with such complicated detail that the all-important qualitative aspects are too deeply concealed.

A more pragmatic technique has thus become increasingly popular, somewhat along the lines of the Galerkin method (see, e.g., ref. 5) of computational fame. One simply introduces a class of analytical forms and imposes enough restrictions to determine uniquely the form required. The difficulty in such an extrapolation method is in a way the complementary problem: there are so few firm restrictions that one is compelled to limit severely the analytic forms. Indeed, reliable microscopic thermodynamic data are pretty much restricted to the particle pair correlations in uniform fluid or derived quantities, in particular the inverse linear response function (see, e.g., ref. 6)

$$\begin{aligned} R(r-r', n) &= \left.\frac{\delta\mu - u(r)}{\delta n(r')}\right|_{n(r)=n} \\ &= \frac{1}{\beta}\left(\frac{\delta(r-r')}{n} - c_2(r-r'; n)\right) \end{aligned} \tag{1.7}$$

where $c_2(r-r'; n)$ is the usual direct correlation function at the uniform density n. In this paper, I will review and considerably enlarge the class of extrapolated analytic forms for the profile and its free energy generator, based upon assumed knowledge of the linear response (1.7). It is well to point out at the start that any approximation method based upon *direct* correlations alone has built-in potential deficiencies—e.g., spatial correlations need not vanish for overlapping hard cores—and I will conclude with a discussion of the extent to which the required additional information can be incorporated.

2. GENERATING FUNCTIONS

A physical theory must of course address relationships between observable quantities. In nonuniform classical fluids, such quantities are restricted in the main to those indicated or sampled by individual particles: the external force field (or potential) and the particle density (for simple fluids). The obvious question to ask concerns the response of the fluid to an imposed potential field $u(r)$.

In the grand canonical ensemble, the grand potential Ω serves as a universal generating function, in the sense that if an observable Q_α occurs linearly in the energy

$$\phi = \phi_0 + \sum \lambda_\alpha Q_\alpha \tag{2.1}$$

then

$$\langle Q_\alpha \rangle = \partial\Omega/\partial\lambda_\alpha \tag{2.2}$$

In particular, the external field energy takes the form $U = \int u(r)\,\hat{n}(r)\,d^3r$, where $\hat{n}(r) = \sum \delta(r - r_i)$ is the dynamical variable whose expectation $\langle \hat{n}(r) \rangle = n(r)$ is the mean density. Hence we have, recalling that $u(r)$ occurs only in the combination $\mu - u(r)$, where μ is the chemical potential,

$$n(r) = -\frac{\delta\Omega}{\delta\mu - u(r)} \tag{2.3}$$

Note, too, that since (2.2) extends to

$$\langle Q_\alpha Q_\beta \rangle - \langle Q_\alpha \rangle \langle Q_\beta \rangle = -\frac{1}{\beta}\frac{\partial^2\Omega}{\partial\lambda_\alpha\,\partial\lambda_\beta} \tag{2.4}$$

then Ω is concave on any parameter set occurring linearly in the energy. As an important special case, the structure factor

$$\begin{aligned} -\frac{1}{\beta}\frac{\delta^2\Omega}{\delta\mu - u(r)\,\delta\mu - u(r')} = \frac{1}{\beta}\frac{\delta n(r)}{\delta\mu - u(r')} &= \langle \hat{n}(r)\,\hat{n}(r') \rangle - n(r)\,n(r') \\ &= n_2(r, r') - n(r)\,n(r') + n(r)\,\delta(r - r') \\ &= S(r, r') \end{aligned} \tag{2.5}$$

is a nonnegative continuous matrix.

The external potential need not be the independent variable of choice. Under two-phase conditions, an infinitesimal change in $u(r)$ causes a dramatic change in $n(r)$, so that it is more reasonable to carry out a Legendre transformation to $n(r)$ as new independent variable,

$$F^\beta[n] = \Omega + \int n(r)[\mu - u(r)]\,d^3r \tag{2.6}$$

and now

$$\mu - u(r) = \delta F^\beta/\delta n(r) \tag{2.7}$$

F^β is the bulk, internal, or residual Helmholtz free energy, i.e., $F - \int n(r)\,u(r)\,d^3r$ and indeed (2.7) transcribes to $\delta F/\delta n(r) = 0$ at fixed $\{u(r)\}$. At fixed density $n(r)$, one has again

$$\langle Q_\alpha \rangle = \partial F^\beta/\partial\lambda_\alpha \tag{2.8}$$

but the analog of (2.4) accumulates correction terms.(7) However, it is true that

$$\begin{aligned}\frac{\delta^2 F^\beta}{\delta n(r)\,\delta n(r')} &= \frac{\delta\mu - u(r)}{\delta n(r')} = -\left(\frac{\delta^2\Omega}{\delta\mu - u\;\delta\mu - u}\right)^{-1}(r, r') \\ &= \frac{1}{\beta}S^{-1}(r, r') = \frac{1}{\beta}\left[\frac{\delta(r-r')}{n(r)} - c_2(r, r')\right] \\ &= \frac{1}{\beta}C(r, r') \end{aligned} \tag{2.9}$$

is nonnegative, F^β being a convex functional of the density.

One might also imagine changing the internal potential. If this is restricted to the pair interaction $\phi(r, r')$, then (2.2) and (2.8) clearly imply that

$$n_2(r, r') = \frac{1}{2}\frac{\delta\Omega}{\delta\phi(r, r')}\bigg|_u = \frac{1}{2}\frac{\delta F^\beta}{\delta\phi(r, r')}\bigg|_n \tag{2.10}$$

It is extremely useful, but rarely practicable, to Legendre transform so that $n_2(r, r')$ takes over as independent variable. Applied to Ω, then, one has

$$\begin{gathered} H[u, n_2] = \frac{1}{2}\iint n_2(r, r')\,\phi(r, r')\,d^3r\,d^3r' - \Omega \\ n(r) = \delta H/\delta\mu - u(r), \qquad \tfrac{1}{2}\phi(r, r') = -\delta H/\delta n_2(r, r') \end{gathered} \tag{2.11}$$

where H is now the enthalpy. Applied to F^β instead, one has

$$\begin{gathered} -kTS[n, n_2] = F^\beta - \frac{1}{2}\iint n_2(r, r')\,\phi(r, r')\,d^3r\,d^3r', \\ \mu - u(r) - \delta kTS/\delta n(r), \; \tfrac{1}{2}\phi(r, r') = \delta kTS/\delta n_2(r, r') \end{gathered} \tag{2.12}$$

where S is the system entropy. I will not further discuss such n_2-transformed ensembles in this paper; there are model systems in which they become manageable.(8)

3. A PRIMITIVE FORM

The relevant sequence in a density-transformed grand ensemble is

$$\mu - u(r) = \delta F^\beta[n]/\delta n(r) \tag{3.1a}$$

$$C(r, r) = \beta R(r, r') = \delta^2\beta F^\beta[n]/\delta n(r)\,\delta n(r') \tag{3.1b}$$

I have suggested that approximations to the profile relation (3.1a) may be developed by using the presumed knowledge of the complete direct correlation (3.1b) in bulk (uniform) fluid as input data. Strictly adhered to, this raises the problem of integrability [since $\mu - u(r)$ is an $n(r)$ derivative, it must satisfy $\delta(\mu - u(r))/\delta n(r') = \delta(\mu - u(r'))/\delta n(r)$], and is most easily avoided by choosing instead to model the free energy F^β itself. It is clear from (3.1a) and (1.4) that F^β in the case of local bulk thermodynamics may be taken as

$$F^\beta[n] = \int n(r)\, f(n(r))\, d^3r \tag{3.2}$$

where $f(n)$ is the bulk specific Helmholtz free energy, satisfying the thermodynamic relation $d(nf) = \mu\, dn$. Proceeding to the van der Waals approximation (1.6), one has instead

$$\begin{aligned} F^\beta[n] = &\int n(r)\, f(n(r))\, d^3r \\ &-\frac{1}{2}\iint n(r)\, \phi_1(r-r')\, n(r')\, d^3r\, d^3r' \end{aligned} \tag{3.3}$$

Let us try to generalize (3.3), which differs from (3.2) by the addition of a term bilinear in the density. If we were to imagine (3.2) as a slow variation approximation, the next order would be expected to bring in a density gradient term, i.e., one linear in the density at a point other than that being observed. We are thus led to investigate a functionally parametric model of the form

$$\begin{aligned} F^\beta[n] = &\int n(r)\, f_0(n(r))\, d^3r \\ &+\frac{1}{2}\iint n(r)\, w(r-r', n(r'))\, d^3r\, d^3r' \end{aligned} \tag{3.4}$$

where, since it is difficult to visualize a reasonable way of avoiding it, we will assume that $w(r, n)$ is of even parity in the vector r. It follows then that

$$\begin{aligned} \mu - u(r_1) = &\ \mu_0(n(r_1)) + \frac{1}{2}\int w(r_1 - r', n(r'))\, d^3r' \\ &+\frac{1}{2}\int n(r)\, w'(r - r_1, n(r))\, d^3r' \\ R(r_1, r_2) = &\ \mu_0'(n(r_1))\, \delta(r_1 - r_2) + \frac{1}{2} w'(r_1 - r_2, n(r_2)) \\ &+\frac{1}{2} w'(r_2 - r_1, n(r_1)) \\ &+\frac{1}{2}\int n(r)\, w''(r - r_1, n(r_1))\, d^3r\, \delta(r_1 - r_2) \end{aligned} \tag{3.5}$$

where primes consistently refer to differentiation with respect to the density argument, and $\mu_0\, dn = d(nf_0)$.

On taking the uniform density limit $n(r) \to n$, we find that (3.4) and (3.5) now reduce to

$$f(n) = f_0(n) + \frac{1}{2} \int w(r, n)\, d^3r \tag{3.6a}$$

$$\mu(n) = \mu_0(n) + \frac{1}{2} \int w(r, n)\, d^3r + \frac{n}{2} \int w'(r, n)\, d^3r \tag{3.6b}$$

$$\begin{aligned} R(r_1 - r_2, n) = {} & \mu_0'(n)\, \delta(r_1 - r_2) + w'(r_1 - r_2, n) \\ & + \frac{n}{2} \int w''(r, n)\, d^3r\, \delta(r_1 - r_2) \end{aligned} \tag{3.6c}$$

with the left-hand sides to be regarded as known bulk data. If w has no δ-function singularity and $w(r, 0) = 0$, then the representation $\beta R(r, n) = (1/n)\, \delta(r) - c_2(r, n)$ coupled with (3.6c) tells us that

$$\beta w'(r, n) = -c_2(r, n) \tag{3.7a}$$

$$\beta \mu_0'(n) + \frac{n}{2} \int \beta w''(r, n)\, d^3r = \frac{1}{n} \tag{3.7b}$$

Integrating (3.7a) and substituting into (3.6b), we have

$$\mu_0(n) = \mu(n) + \frac{1}{2\beta} \frac{\partial}{\partial n} \left[n \iint_0^n c_2(r, n')\, dn'\, d^3r \right] \tag{3.8}$$

which by virtue of the well-known relation $\mu'(n) = \int R(r, n)\, d^3r$ is seen to imply (3.7b) as well. Furthermore, (3.6a) results from integration of (3.6b), and can now be written as

$$f_0(n) = f(n) + \frac{1}{2\beta} \iint_0^n c_2(r', n')\, dn'\, d^3r' \tag{3.9}$$

We can therefore conclude by substituting (3.9) and the integrated (3.7a) into (3.4) to obtain the expression

$$\begin{aligned} F^\beta[n] = {} & \int n(r)\, f(n(r))\, d^3r \\ & + \frac{1}{2\beta} \iint n(r) \int_{n(r')}^{n(r)} c_2(r - r', n)\, dn\, d^3r\, d^3r' \end{aligned} \tag{3.10}$$

which duly incorporates all of the bulk information. Of course, the profile equation

$$\mu - u(r) = \mu(n(r)) + \frac{1}{2\beta}\int_{n(r')}^{n(r)} c_2(r-r', n)\, dn\, d^3r'$$
$$+ \frac{1}{2\beta}\int [n(r) - n(r')]\, c_2(r-r', n(r))\, d^3r' \tag{3.11}$$

follows at once. This is very much in the same family as that considered by Ebner *et al.*(9) and is immediately applicable to substrate-bounded fluids. However, it also encounters the difficulty that two-phase interfaces require bulk information at unphysical interphase densities. Presumably, this should be obtained by following a van der Waals loop, which does correspond to constrained uniformity.(10)

4. ASSOCIATED MODELS

Since the particular form (3.4) is notably nonunique, many other possibilities have been suggested. Meister and Kroll(11) developed the conceptually elegant idea of expanding the density profile about a slowly varying reference, which was then determined by imposing the condition of minimum sensitivity on the free energy. Groot and Van der Eerden(12) then extended this free energy to the model form

$$F^{\beta} = \frac{1}{\beta}\int n(r)[\ln n(r) - 1]\, d^3r + \int n(r)\, f^{\mathrm{ex}}(\bar{n}(r))\, d^3r$$
$$- \frac{1}{2}\iint n(r)[n(r') - \bar{n}(r)]\, w(r-r', \bar{n}(r))\, d^3r\, d^3r' \tag{4.1}$$

where f^{ex} is the excess specific free energy for the uniform fluid and $\bar{n}(r)$ plays the role of reference density. Making (4.1) stationary with respect to $\bar{n}(r)$ and imposing the reproduction of the bulk direct correlation then yields the interrelations

$$\begin{gathered} \int w'(r-r', \bar{n}(r))[n(r') - \bar{n}(r)]\, d^3r' = 0 \\ \tilde{c}_{2,k}(n) = \tilde{w}_k(n) + \frac{n}{\tilde{w}_0(n)}\,[\tilde{w}'_k(n)]^2 \end{gathered} \tag{4.2}$$

where $\tilde{f}_k$ denotes the Fourier transform of $f(r)$.

The model (4.1) can also count among its ancestors a number of approaches in extended mean field format. Typical is that of Tarazona and Evans(13) (see also Mederos *et al.*(14)), in which one sets

$$F^{\beta} = \frac{1}{\beta} \int n(r)[\ln n(r) - 1]\, d^3r + \int n(r)\, f_0^{\text{ex}}(\bar{n}(r))\, d^3r$$
$$-\frac{1}{2} \iint n(r)\, n(r')\, \phi_1(r - r')\, d^3r\, d^3r' \tag{4.3}$$

where $f_0^{\text{ex}}(n)$ denotes the excess free energy for the core fluid, $-\phi_1$ is the tail potential, and

$$\bar{n}(r) = \int \varepsilon(a - |r - r'|)\, d^3r'/(\tfrac{4}{3}\pi a^3) \tag{4.4}$$

averages over the diameter-a core of the core fluid. Perhaps the earliest version, that of Nordholm *et al.*,(15) used the basic excluded-volume van der Waals equation approximation $f_0^{\text{ex}}(n) = -\ln(1 - n\frac{3}{4}\pi a^3)$. More recently, Baus[16] replaced the $\varepsilon(a - |r - r'|)$ in (4.4) by the zero-density Mayer function $\exp[-\beta\phi(r - r')]$.

Another sequence of model free energies has been proposed in which advantage is taken of the existence of exact solutions for a very small number of model fluids. Prototypical is the one-dimensional hard rod fluid, for which one finds the exact result(17)

$$F^{\beta} = \frac{1}{\beta} \int n(x)[\ln n(x) - 1]\, dx + \int n_{\sigma}(x)\, f^{\text{ex}}(n_{\tau}(x))\, dx \tag{4.5}$$

where

$$f^{\text{ex}}(n) = -\frac{1}{\beta} \ln(1 - na)$$

$$n_{\sigma}(x) = \frac{1}{2}\left[n\left(x + \frac{1}{2}a\right) + n\left(x - \frac{1}{2}a\right)\right], \qquad n_{\tau}(x) = \frac{1}{a} \int_{x - a/2}^{x + a/2} n(y)\, dy$$

Here f^{ex} is of course the exact bulk specific free energy. The appearance of the linear "surface" and "volume" averages n_{σ} and n_{τ} is striking, suggesting that an arbitrary three-dimensional nonuniform fluid be modeled by the analogous expression, in which appropriate averages

$$\begin{aligned} n_{\sigma}(r) &= \int \sigma(r - r')\, n(r')\, d^3r' \\ n_{\tau}(r) &= \int \tau(r - r')\, n(r')\, d^3r' \end{aligned} \tag{4.6}$$

are inserted. The problem is that of the determination of the weight functions σ and τ. When "surface" and "volume" are meaningful concepts, such as in a hard sphere fluid, it is reasonable to choose

$$\begin{aligned} n_\sigma(r) &= \frac{1}{\pi a^2} \int_{|r-r'|=a/2} n(r')\, dS' \\ n_\tau(r) &= \frac{6}{\pi a^3} \int_{|r-r'|\leqslant a/2} n(r')\, d^3r' \end{aligned} \tag{4.7}$$

This was carried out by Robledo,$^{(18)}$ who showed that known bulk properties were reproduced to decent accuracy.

If one wants to take explicit advantage of known bulk data on direct correlations, σ and τ cannot be chosen at will. Indeed, by differentiating the three-dimensional version of (4.5) twice with respect to density, which is then set to uniformity, n, one finds$^{(19)}$

$$\begin{aligned} c_2(r_1-r_2, n) = {} & -2B_2(n) \int \sigma(r_1-r)\, \tau(r_2-r)\, d^3r \\ & - nB_2'(n) \int \tau(r_1-r)\, \tau(r_2-r)\, d^3r \end{aligned} \tag{4.8}$$

where $B_2(n) = [\beta P(n) - n]/n^2$. The knowledge of c_2 at two reference densities can be used to determine the two functions σ and τ (most readily via Fourier transform). If the surface–volume interpretation is taken more seriously, one can impose the scaling condition$^{(20)}$

$$\sigma(r) = \frac{1}{3} \frac{\partial}{\partial \lambda} \tau\left(\frac{r}{\lambda}\right)\bigg|_{\lambda=1} \tag{4.9}$$

and so have just one reference density to employ. But the availability of two densities is certainly useful if a two-phase system—primarily at two densities—is being studied. In fact, the clear disadvantage of the generalized (4.5) is that one cannot make use of knowledge of the direct correlations over the full range of densities.

5. RANK-ONE REPRESENTATION

The exactly solvable hard rod fluid has another suggestive consequence. If one computes the nonuniform inverse linear response by two differentiations of (4.5), there results$^{(17)}$

$$\begin{aligned} C(x, x') &= \frac{\delta(x-x')}{n(x)} - c_2(x, x') \\ &= \int q(x'', x)\, n(x'')\, q(x'', x')\, dx'' \end{aligned} \tag{5.1}$$

where

$$q(x'', x) = \delta(x - x'')/n(x) + \varepsilon(x - x'')\, \varepsilon(x'' - x + a) \Big/ \left[1 - \int_{x''}^{x'' + a} n(z)\, dz \right]$$

ε as usual denotes the Heaviside step function. In operator form, (5.1) reads $C = q^{+} n q$, consistent with the observation (2.9) that C is a non-negative operator, and an obvious extension of the Wertheim–Baxter$^{(21,22)}$ k-space decomposition

$$\tilde{C}_k = \tilde{Q}_k^* \tilde{Q}_k \tag{5.2}$$

To see what this expression might indeed suggest, let us, following the hint of (4.5), write F^{β} as a general function of linear averages:

$$\beta F^{\beta}[n] = \int \Phi(n_1(r), n_2(r), \ldots)\, d^3 r \tag{5.3}$$

where

$$n_{\alpha}(r) = \int \tau_{\alpha}(r - r')\, n(r')\, d^3 r'$$

We assume that τ_{α} is normalized to unity, so that $n_{\alpha}(r) = n$, where $n(r) = n$. It follows at once by differentiation that

$$\beta(\mu - u(r)) = \int \sum_{\alpha} \hat{\tau}_{\alpha}(R - r)\, \Phi'_{n_{\alpha}}(\cdots n_{\gamma}(r) \cdots)\, d^3 R \tag{5.4a}$$

and then that

$$C(r, r') = \sum_{\alpha, \beta} \int \tau_{\alpha}(R - r)\, \tau_{\beta}(R - r')\, \Phi''_{n_{\alpha} n_{\beta}}(\cdots n_{\gamma}(R) \cdots)\, d^3 R \tag{5.4b}$$

This shows that for a uniform fluid,

$$\tilde{C}_k(n) = \sum \Phi''_{n_{\alpha} n_{\beta}}(n)\, \tilde{\tau}^*_{\alpha,k} \tilde{\tau}_{\beta,k} \tag{5.5}$$

which, as n varies, lies in the vector space spanned by the functions of k, $\{\tilde{\tau}^*_{\alpha,k} \tilde{\tau}_{\beta,k}\}$. In order to achieve the form (5.2), it is sufficient to arrange the definitions of the τ_{α} so that

$$\Phi''_{n_{\alpha} n_{\beta}}(n) = K_{\alpha}(n)\, K_{\beta}(n) \tag{5.6}$$

for real K_{α}, i.e., to choose the τ_{α} and $K_{\alpha}(n)$ to satisfy

$$\tilde{Q}_k(n) = \sum K_{\alpha}(n) \tilde{\tau}_{\alpha,k} \tag{5.7}$$

We can thus assume that the $K_\alpha(n)$ and $\tilde{\tau}_\alpha$ are known. The multivariable function $\Phi(\cdots n_\gamma(r)\cdots)$ is, to be sure, not then determined by (5.6). But if we extend (5.6) to the rank-one requirement

$$\Phi''_{n_\alpha n_\beta}(\cdots n_\gamma \cdots) = K_\alpha(\cdots n_\gamma \cdots)\, K_\beta(\cdots n_\gamma \cdots) \tag{5.8}$$

where $K_\alpha(n, n, \ldots) = K_\alpha(n)$, then the nonuniform (5.4b) factorizes as well,

$$C(r, r') = \int \sum_\alpha K_\alpha(\cdots n_\gamma(R) \cdots)\, \tau_\alpha(R - r) \times \sum_\beta K_\beta(\cdots n_\gamma(R) \cdots)\, \tau_\beta(R - r')\, d^3 r' \tag{5.9}$$

and little arbitrariness remains. To solve (5.8), we observe that since the Jacobian matrix $[(\partial/\partial n_\alpha)(\partial\Phi/\partial n_\beta)]$ is of rank one, then the $\partial\Phi/\partial n_\beta$ are all functionally related, and we can write

$$\partial\Phi/\partial n_\alpha = g_\alpha(v) \tag{5.10}$$

for some unknown function v. Let us define

$$\Phi = -P + \sum n_\beta\, g_\beta(v) \tag{5.11}$$

Then

$$\partial P/\partial n_\alpha = -\partial\Phi/\partial n_\alpha + g_\alpha(v) + \sum n_\beta\, g'_\beta(v)\, \partial v/\partial n_\alpha = \left[\sum n_\beta\, g'_\beta(v)\right] \partial v/\partial n_\alpha$$

so that the two-column matrix $[\partial P/\partial n_\alpha, \partial v/\partial n_\alpha]$ is of rank one. It follows that $P = P(v)$, whence

$$\Phi = \sum n_\beta\, g_\beta(v) - P(v) \tag{5.12}$$

Furthermore, since

$$\sum n_\beta\, g'_\beta(v)\, \partial v/\partial n_\alpha = \partial P(v)/\partial n_\alpha = P'(v)\, \partial v/\partial n_\alpha$$

we have the relation

$$P'(v) = \sum n_\beta\, g'_\beta(v) \tag{5.13}$$

Returning to (5.10), we see that

$$\partial^2\Phi/\partial n_\alpha\, \partial n_\beta = g'_\beta(v)\, \partial v/\partial n_\alpha = K_\alpha K_\beta$$

implying that

$$\partial v/\partial n_\alpha = K_\alpha / w, \qquad g'_\alpha(v) = K_\alpha w \tag{5.14}$$

for some w. Now we can assume without loss of generality that the function v reduces to n when all $n_\sigma = n$: $v(n, n,...) = n$. Hence $\sum \partial v/\partial n_\alpha = 1$ at common n, or $w(n, n,...) = \sum K_\alpha(n)$, from which

$$g'_\alpha(n) = K_\alpha(n) \sum K_\beta(n) \tag{5.15}$$

At common $n = v$, (5.13) now reads

$$P'(v) = v \sum g'_\beta(v) \tag{5.16}$$

Hence (5.13), (5.15), and (5.16) determine the function v by the implicit relation

$$\sum (n_\beta - v) K_\beta(v) = 0 \tag{5.17}$$

There remains only the transcription of (5.12), according to (5.12), (5.15), and (5.16), as

$$\Phi(\cdots n_\gamma \cdots) = \int^v \sum_\alpha K_\alpha(n) \sum_\beta (n_\beta - n) K_\beta(n)\, dn \tag{5.18}$$

which is the desired result.

It is not necessary to find the decomposition (5.7) explicitly. From (5.7), we have

$$Q(r, n) = \sum K_\alpha(n)\, \tau_\alpha(r) \tag{5.19}$$

It follows that

$$\begin{gathered} \int Q(r, n)\, d^3r = \sum K_\alpha(n) \\ \int Q(r - r', n)\, n(r')\, d^3r' = \sum K_\alpha(n)\, n_\alpha(r) \end{gathered} \tag{5.20}$$

so that (5.17) and (5.18) reduce to

$$\Phi[n] = \int^{v(r)} \iint Q(r - r', n)[n(r') - n]\, Q(r'', n)\, d^3r'\, d^3r''\, dn \tag{5.21}$$

where

$$\int Q(r - r', v(r))[n(r') - v(r)]\, d^3r' = 0$$

For example, in the case of hard rods, where

$$Q(x, n) = \frac{\delta(x)}{n^{1/2}} + \frac{\varepsilon(x+a)\,\varepsilon(-x)}{1-na}\,n^{1/2} \tag{5.22}$$

the ν equation is readily solved as

$$\nu(x) = \frac{n(x)}{1 + an(x) - \int_x^{x+a} n(y)\,dy} \tag{5.23}$$

and Φ then integrates without difficulty to

$$\Phi[n] = n(x) \ln \frac{n(x)}{1 - \int_x^{x+a} n(y)\,dy} - n(x) \tag{5.24}$$

whose spatial integral is identical to (4.5).

But in fact the formulation is not entirely satisfactory. We see from (5.14) that $K_\alpha = [g'_\alpha(\nu)\,\partial\nu/\partial n_\alpha]^{1/2}$; on differentiating (5.17), we find

$$\partial\nu/\partial n_\alpha = K_\alpha(\nu) \Big/ \sum_\nu [K_\gamma(\nu) - (n_\nu - \nu)\,K'_\gamma(\nu)]$$

Thus, on inserting (5.15),

$$K_\alpha = K_\alpha(\nu) \left(\frac{\sum K_\gamma(\nu)}{\sum K_\gamma(\nu) - (\nu_\gamma - \nu)\,K'_\gamma(\nu)} \right)^{1/2} \tag{5.25}$$

The singular part of $C(r, r')$, we know, must have the form $\delta(r-r')/n(r)$, so that we can always imagine $\tau_0(r) = \delta(r)$, with $K_0 = n_0(r)^{-1/2}$. While certainly $K_0(n) = n^{-1/2}$, it seems clear from (5.25) that one cannot rely on obtaining $K_0 = n_0^{-1/2}$. Therefore, the singular part of the linear response is simply wrong, and something must be done. Of course, this defect is not uncommon; it affects models ranging from the original van der Waals (3.3), to the generalized VdW of Nordholm and Haymet,(23) on to more sophisticated attempts such as that of Mazuruk *et al.*(24) It is nonetheless deplorable.

6. RANK-TWO REPRESENTATION

To repair the possible inadequacy of the ansatz (5.8), let us return to exactly solved models. An extremely simple one serves as entree; it does involve many-body forces, but that is irrelevant in the present format. In this model, one has

$$\beta F^B = \int n(r)[\ln n(r) - 1]\,d^3r - \frac{1}{2} \iint n(r)\,c(r-r')\,n(r')\,d^3r\,d^3r' \tag{6.1}$$

and it can be verified$^{(25)}$ that there is an underlying many-body potential energy providing that $c(r-r') \geqslant 0$, or, in the infinite-dimensional case, for any short-range repulsive two-body interaction.$^{(26)}$ We have at once from (6.1) the Debye–Hückel-like

$$\beta(\mu - u(r)) = \ln n(r) - \int c(r-r')\, n(r')\, d^3r' \tag{6.2}$$

and the extremely simple linear response

$$c_2(r, r') = c(r-r') \tag{6.3}$$

But (6.3) is significant. It states that

$$C(r, r') = \frac{\delta(r-r')}{n(r)} - c(r-r') \tag{6.4}$$

which shows at once that the rank-one form (5.9) cannot hold, whereas rank two, e.g., in the form

$$\begin{aligned} C(r, r') = \int & \left[n(r)^{-1/2}\, \delta(r-R) - \frac{1}{2} n(r)^{1/2}\, c(r-R) \right] \\ & \times \left[n(r')^{-1/2}\, \delta(r'-R) - \frac{1}{2} n(r')^{1/2}\, c(r'-R) \right] d^3R \\ & - \frac{1}{4} \int n(r)^{1/2}\, c(r-R)\, n(r')^{1/2}\, c(r'-R)\, d^3R \end{aligned} \tag{6.5}$$

is perfectly fine. Equation (6.5) points out, incidentically, that the nonnegativity of the operator $C(r, r')$ may be a consequence of the restricted density range permitted, and need not be manifest.

A further hint of the underlying structure is afforded by the observation that (5.1), which led to the formalism represented by (5.9), employs a factor $Q(x, n)$ of (5.19), depending upon the nonsymmetric weight function

$$\tau(x-x') = (1/a)\, \varepsilon(x-x'+a)\, \varepsilon(x'-x)$$

The breaking of parity in one dimension is not very serious, but raises substantial problems in three dimensions. To bring this issue into sharper focus, let us recall the factorization structure (5.2) of the hard sphere fluid in PY approximation. One finds$^{(21,22)}$

$$\tilde{Q}_k = K_0(n)\, \tilde{\tau}_{0,k} + K_1(n)\, \tilde{\tau}_{1,k} + K_2(n)\, \tilde{\tau}_{2,k} \tag{6.6}$$

where

$$\tilde{\tau}_{0,k}=1, \qquad \tilde{\tau}_{1,k}=-2(e^{-ika}-1+ika)/(ka)^2$$
$$\tilde{\tau}_{2,k}=-6i(e^{-ika}-1+ika+\tfrac{1}{2}k^2a^2)/(ka)^3$$
$$K_0(n)=n^{-1/2}, \qquad K_1(n)=\frac{3}{n^{1/2}}\frac{\eta(2+\eta)}{(1-\eta)^2}, \qquad K_2(n)=\frac{2}{n^{1/2}}\frac{\eta(1+2\eta)}{(1-\eta)^2} \tag{6.7}$$
$$\eta=n\pi a^3/6$$

Now the one-dimensional Fourier transforms of the $\tilde{\tau}_{i,k}$ are indeed of the core range a, but the three-dimensional transforms mandatory for a nonuniform fluid,

$$\tau(r)=\frac{1}{2\pi^2 r}\int_0^\infty \tilde{\tau}_k k \sin kr\, dk \tag{6.8}$$

oscillate forever, directly attributable to the odd imaginary part of $\tilde{\tau}_k$.

The remedy is clear. We write

$$\tilde{\tau}_k=\tilde{\tau}'_k-ik\tilde{\tau}''_k \tag{6.9}$$

and correspondingly

$$\tilde{Q}_k=\tilde{Q}'_k-ik\tilde{Q}''_k \tag{6.10}$$

where $\tilde{Q}'_k$ and $\tilde{Q}''_k$ are real, even functions of k. Then

$$\tilde{C}_k=(\tilde{Q}'_k)^2+k^2(\tilde{Q}''_k)^2=\tilde{Q}'_k\tilde{Q}'_k+(ik\tilde{Q}''_k)(-ik\tilde{Q}''_k) \tag{6.11}$$

which is the square of a scalar plus the square of a vector, a generalized rank-two decomposition. In particular, in the PY case, we have

$$\tilde{C}(k)=[K_0(n)\tilde{\tau}_{0,k}+K_1(n)\tilde{\tau}_{3,k}+K_2(n)\tilde{\tau}_{4,k}]^2$$
$$+\left|\frac{a}{3}K_1(n)\widetilde{\nabla\tau_{4,k}}-\frac{9}{4}k_2(n)\widetilde{\nabla\tau_{5,k}}\right|^2 \tag{6.12}$$

where

$$\tilde{\tau}_{3,k}=2(1-\cos ka)/(ka)^2, \qquad \tilde{\tau}_{4,k}=-6(\sin ka-ka)/(ka)^2$$
$$\tilde{\tau}_{5,k}=-24(\cos k_a-1+\tfrac{1}{2}k^2a^2)/(ka)^4$$

Generalization of (5.6) to the rank-two case is somewhat involved, and will be reported in a later publication. A more specialized form in which rank two occurs in a natural way is given by

$$\beta F^B = \int n(r)[\ln n(r) - 1 - \ln \psi(R)]\, d^3R \tag{6.13}$$

for we can then write

$$\beta(\mu - u(r)) = \ln n(r) - \ln \psi(r) - \int \frac{n(R)}{\psi(R)} \frac{\delta\psi(R)}{\delta n(r)}\, d^3R \tag{6.14}$$

as well as, after a slight rearrangement,

$$\begin{aligned} C(r, r') = \int & \left(\frac{\delta(r-R)}{n(R)^{1/2}} - \frac{n(R)^{1/2}}{\psi(R)} \frac{\delta\psi(R)}{\delta n(r)}\right) \\ & \times \left(\frac{\delta(r'-R)}{n(R)^{1/2}} - \frac{n(R)^{1/2}}{\psi(R)} \frac{\delta\psi(R)}{\delta n(r')}\right) d^3R \\ & - \int \frac{n(R)}{\psi(R)} \frac{\delta^2\psi(R)}{\delta n(r)\, \delta n(r')}\, d^3R \end{aligned} \tag{6.15}$$

with precisely the correct singularity structure. Again, it is convenient to imagine that the n dependence of $\psi(R)$ occurs locally via the nonlocal

$$n_\alpha(R) = \int \tau_\alpha(R - r')\, n(r')\, d^3r' \tag{6.16}$$

but to distinguish two types of τ_α, the scalars in which

$$\alpha \in S: \quad \int \tau_\alpha(R)\, d^3R = 1 \tag{6.17}$$

and the vector, i.e., gradient, components, in which

$$\alpha \in V: \quad \int \tau_\alpha(R)\, d^3R = 0 \tag{6.18}$$

Then, in obvious notation,

$$\begin{aligned} C(r, r') = \int & \left[\frac{\delta(r-R)}{n(R)^{1/2}} - \sum_\alpha \frac{n(R)^{1/2}}{\psi} \psi'_\alpha \tau_\alpha(r-R)\right] \\ & \times \left[\frac{\delta(r'-R)}{n(r)^{1/2}} - \sum_\beta \frac{n(R)^{1/2}}{\psi} \psi'_\beta \tau_\beta(r'-R)\right] d^3R \\ & - \int \sum_{\alpha,\beta} \frac{n(R)}{\psi} \psi''_{\alpha,\beta} \tau_\alpha(r-R)\, \tau_\beta(r'-R)\, d^3R \end{aligned} \tag{6.19}$$

reducing in the uniform case to

$$\tilde{C}_k = \left[n^{-1/2} - \sum_{\alpha} \frac{n^{1/2}}{\psi(n, 0)} \psi'_{\alpha}(n, 0) \tilde{\tau}_{\alpha,k} \right]^* \\ \times \left[n^{-1/2} - \sum_{\beta} \frac{n^{1/2}}{\psi(n, 0)} \psi'_{\beta}(n, 0) \tilde{\tau}_{\beta,k} \right] \\ - \frac{n}{\psi(n, \alpha)} \sum_{\alpha,\beta} \psi''_{\alpha\beta}(n, 0) \tilde{\tau}^*_{\alpha,k} \tilde{\tau}_{\beta,k} \tag{6.20}$$

where the arguments of ψ symbolize the fact that $n_\alpha \to n$ for $\alpha \in S$, $n_\alpha \to 0$ for $\alpha \in V$.

We now have to extend the analysis of Section 5. Since a gradient can appear in ψ only when dotted with another gradient, we will certainly have $\psi'_\alpha(n, 0) = 0$ for $\alpha \in V$, as well as $\psi''_{\alpha\beta}(n, 0) = 0$ for $\alpha \in S$, $\beta \in V$ or vice versa. Hence, assuming a three-dimensional $SS + V \cdot V$ rank-two form, we will have to compare (6.19) with input bulk data appearing as

$$\tilde{C}_k = \left[n^{-1/2} - n^{1/2} \sum_{\alpha \in S} S_\alpha(n) \tilde{\tau}_{\alpha,k} \left(n^{-1/2} - n^{1/2} \sum_{\beta \in S} S_\beta(n) \tilde{\tau}_{\beta,k} \right) \right] \\ + n \left[\sum_{\alpha \in V} V_\alpha(n) \tilde{\tau}_{\alpha,k} \right]^* \left[\sum_{\beta \in V} V_\beta(n) \tilde{\tau}_{\beta,k} \right] \tag{6.21}$$

The simplest assumption, with attendant disadvantages which will soon appear, is that the rank-one character of the second part of (6.21) extends to the nonuniform case. Thus, we require

$$\psi''_{\alpha,\beta}/\psi = -Q_\alpha Q_\beta \tag{6.22}$$

with the boundary conditions

$$\begin{gathered} \psi'_\alpha(n, 0)/\psi(n, 0) = S_\alpha(n) \qquad \text{for} \quad \alpha \in S \\ Q_\alpha(n, 0) = 0 \qquad \text{for} \quad \alpha \in S, \qquad Q_\alpha(n, 0) = V_\alpha(n) \qquad \text{for} \quad \alpha \in V \end{gathered} \tag{6.23}$$

Proceeding then as in Eqs. (5.9)–(5.13), we find from (6.22) that

$$\partial\psi/\partial n_\alpha = g_\alpha(v) \tag{6.24}$$

for suitable v, which will now be fixed by imposing the condition $P(v) = -v$ (since P no longer denotes pressure in the present context). We therefore define

$$\psi = \sum n_\alpha g_\alpha(v) - v \tag{6.25}$$

and condition (6.24) readily reduces to the single condition

$$1 = \sum n_\alpha g'_\alpha(v) \tag{6.26}$$

which determines v and guarantees (6.22), with the identification [using $\partial v/\partial n_\beta = -g'_\beta(v)/\sum n_\alpha g''_\alpha(v)$]

$$Q_\alpha^2 = g'_\alpha(v)^2 \Big/ \left[\sum n_\alpha g''_\alpha(v)\right]\left[\sum n_\alpha g_\alpha(v) - v\right] \tag{6.27}$$

The functions $g_\alpha(v)$ are then to be determined from the boundary conditions, which reduce to

$$\begin{gathered}\frac{g_\alpha(v(n,0))}{n\sum_{\beta\in S} g_\beta(v(n,0)) - v(n,0)} = S_\alpha(n), \qquad \alpha \in S\\ \left.\frac{g'_\alpha(v)}{[\sum_\beta n_\beta g''_\beta(v)]^{1/2}}\right|_{\{n_\alpha\}\to(n,0)} \frac{1}{[n\sum_{\beta\in S} g_\beta(v(n,0)) - v(n,0)]^{1/2}}\\ = \begin{cases} 0, & \alpha \in S\\ V_\alpha(n), & \alpha \in V\end{cases}\end{gathered} \tag{6.28}$$

It is clear that (6.28) are self-consistent only if $v(n, 0) = c$ is some n-independent constant, that the $S_\alpha(n)$ have a common structure $(an + b)^{-1}$ to within proportionality, and that the $V_\alpha(n)$ similarly have a common structure. Thus, the simplified treatment based upon (6.22) is restricted, as was the extension of (4.5), to a density domain small enough that such a representation is reasonable [in which case the $g_\alpha(v)$ are highly underdetermined]. A true higher rank representation is called for.

7. DISCUSSION

The task of extrapolating from a spectrum of bulk data to the behavior of a nonuniform fluid requires that a course be steered between overdetermination and underdetermination. At the direct correlation function level, we have seen that as soon as one passes beyond the basic extrapolation (3.10), one may fail to include other than a small selection of bulk data [(4.5) and the following, or (6.28)], the basic δ-function singularity may only be approximated [Eq. (5.15)], or the short-range direct correlations may be inadequately represented [Eq. (4.4)]. In fact, none of these techniques even attempts to reproduce the short-range density correlations when known, e.g., the vanishing distribution when hard cores overlap, or the possibility of collective modes contributing to anomalous long-range correlations such as those associated with self-maintained interfaces.(4) In the abstract, there is no problem: one simply includes enough functional generality in the free energy ansatz—but not too much—to accommodate the additional data.

The hard core overlap case is an example of independent data which might be used for fine tuning. It is a special case of an independent relationship involving the density correlation function, the simplest of which is the second of the YBG hierarchy

$$\nabla n(r) + n(r)\,\nabla\beta(r) + \int n_2(r, r')\,\nabla\phi(r, r')\,d^3r' = 0 \tag{7.1}$$

for known guaranteed two-body interaction $\phi(r, r')$. Although (7.1) has not been used in precisely the fashion suggested above, its obvious relation to (2.7), in the readily derivable form(27,28)

$$\nabla n(r) + n(r)\,\nabla\beta u(r) = \int c_2(r, r')\,\nabla n(r')\,d^3r' \tag{7.2}$$

with c_2 of the generalized (4.5), has led(29) to interesting closure approximations.

A possibility which has been examined is that of inserting correlation function information directly into the free energy ansatz. For example, Curtin and Ashcroft(30) made use of (2.10) to turn the interaction up from zero to its final value: $\phi_\lambda(r, r') = \lambda\phi(r, r')$, whence

$$\begin{aligned} F^B(n) &= F_0^B[n] + \int_0^1 \frac{\partial F_\lambda^B[n]}{\partial\lambda}\,d\lambda \\ &= F_0^B(r) + \iiint_0^1 \frac{\partial\phi_\lambda(r, r')}{\partial\lambda}\,\frac{\delta F_\lambda^B[n]}{\delta\phi_\lambda(r, r')}\,d\lambda\,d^3r\,d^3r' \\ &= F_0^B[n] + \frac{1}{2}\iint n(r)\,n(r')\,\phi(r - r')\int_0^1 g_\lambda(r, r')\,d\lambda\,d^3r\,d^3r' \end{aligned} \tag{7.3}$$

However, they then made the ansatz

$$\begin{aligned} &\phi(r - r')\int_0^1 g_\lambda(r, r')\,d\lambda \\ &\quad \to w(r - r'; \rho(r))\int \phi(r - r'')\int_0^1 g_\lambda(r - r''; \rho(r))\,d\lambda\,d^3r'' \end{aligned} \tag{7.4}$$

in terms of the bulk correlation g at density $\rho(r)$, where

$$\rho(r) = \int w(r - r'; \rho(r))\,n(r')\,d^3r' \tag{7.5}$$

Thus, although demanding reproduction of bulk direct correlations gives quite decent results, the short-range restrictions enforced by the factor $\phi(r-r')$ are lost.

Even more severe requirements can be adopted. Since $F^B[n]$ generates *all* direct correlations and therefore all correlations, further members of the YBG hierarchy could be used as well. In fact, it would be interesting to use the direct correlations from an F^B ansatz to close the YBG sequence without bothering to demand identity of bulk data. Such approaches, which seem computationally feasible, have not been implemented.

Finally, there is the long-range correlation problem, which has indeed been faced, if only from behind. The point is that, if, instead of a nonuniform ansatz reproducing bulk distribution data, one only asks that it mimic a reference, e.g., hard core system, then the remaining interaction can be appended as a mean field term—see (3.3). In such a case, self-inconsistent long-range correlations along an interface will indeed be produced. But sufficient conditions to accomplish this in a self-consistent fashion have not yet been enunciated. The field is clearly in its early stages.

ACKNOWLEDGMENTS

The paper was based upon lectures given at Cocoyoc, Mexico, January 1982, and Edinburgh, Scotland, July 1983. This research was supported in part by NSF grant CHE086-07598 and DOE contract DE-AC02-76ER03077.

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