

Some Solvable Models of Nonuniform Classical Fluids

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A model classical fluid is constructed by assuming that the direct correlation function $c(\mathbf{r}-\mathbf{r}')$ is independent of any applied external field. Thermodynamic consistency requires that $c(\mathbf{r}-\mathbf{r}') \geq 0$, and permits explicit representation of the model by a many-body interaction potential. In the canonical ensemble, the model shows a phase transition to an infinite density condensed phase, but in the grand canonical ensemble only an anomalous transition to zero density vapor is found to stably exist.

KEY WORDS: Nonuniform fluid; density functional; many-body forces; phase transition.

1. INTRODUCTION

The study of simple classical fluids has in many ways reached maturity, with reliable information on states of thermal equilibrium available over a wide range of thermodynamic parameters. However, such an assessment does not apply to highly nonuniform fluids. Many approximations now exist, but their reliability remains a source of uncertainty. One course of action under these circumstances is the construction of model systems that can be solved exactly, to serve as references and for testing approximations. To be sure, models must be equipped with certain peculiarities to permit their ready solution. A few simple one-dimensional models have been solved,⁽¹⁾ and even a special two-dimensional one.⁽²⁾ In this paper, we shall consider a class of models of unrestricted dimensionality, but with a tightly

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connected set of many-body potentials, somewhat different in spirit from those of one-dimensional cluster models,⁽³⁾ being based instead on a realization of one of the approximations in current use.

2. THE BASIC MODEL

The problem we consider is this: Suppose that the reciprocal temperature β and interactions, pair, triplet, and otherwise, of a classical fluid in the grand ensemble are fixed. What then is the relationship between an applied external potential $u(\mathbf{r})$ and the resulting density $n(\mathbf{r})$? We may imagine that full knowledge of the uniform system at all bulk densities is available, e.g. pair distribution $n_2(\mathbf{r}, \mathbf{r}')$, triplet distribution $n_3(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, ..., and if *their* changes under nonuniformity were known, the system could readily be solved. Indeed, many approximations amount to pinpointing some 2-particle distribution which is to be regarded as not changing at all when the system is made nonuniform. A question we may ask is whether any such approximation is consistent with a model fluid with *some* set of interactions.

One approximation that has been used for systems with a known predominant density, e.g., a fluid bounded by a substrate, is that the "radial distribution"

$$g(\mathbf{r}_1, \mathbf{r}_2) = n_2(\mathbf{r}_1, \mathbf{r}_2)/n(\mathbf{r}_1) n(\mathbf{r}_2) \quad (2.1)$$

maintains its reference bulk value under an applied external field.⁽⁴⁾ This can be used as closure for the first of the YBG hierarchy

$$\nabla n(\mathbf{r})/n(\mathbf{r}) + \nabla \beta u(\mathbf{r}) + \int \nabla \beta \phi(\mathbf{r} - \mathbf{r}') g(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d^3 r' = 0 \quad (2.2)$$

when only a pair interaction $\phi(\mathbf{r} - \mathbf{r}')$ is present. It can also be used as closure for the interaction-independent linear response relation⁽⁵⁾

$$\nabla n(\mathbf{r})/n(\mathbf{r}) + \nabla \beta u(\mathbf{r}) + \int \nabla \beta u(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d^3 r' = 0 \quad (2.3)$$

(or with $h = g - 1$ replacing g —these are equivalent) for any—even many-body—interaction that is translation invariant. However, invariance of g in (2.1) is valid only for an ideal gas. We simply apply the operation $\delta/\delta - \beta u(\mathbf{r}'')$ to (2.1), leading after a small amount of distribution algebra to

$$n_3(1, 2, 3) = \frac{n_2(1, 2) n_2(2, 3)}{n(2)} + \frac{n_2(1, 2) n_2(1, 3)}{n(1)} - n_2(1, 2) n(3) \quad (2.4)$$

in obvious notation. It is easy to see that the right-hand side of (2.4) is not symmetric in particles 1, 2, 3 unless $g(1, 2) = \text{const}$, and so the invariance of g applies to no nontrivial fluid.

The linear response relation (2.3) can also be written as

$$\nabla n(\mathbf{r})/n(\mathbf{r}) + \nabla \beta u(\mathbf{r}) = \int c_2(\mathbf{r}, \mathbf{r}') \nabla n(\mathbf{r}') d^3 r' \quad (2.5)$$

where $c_2(\mathbf{r}, \mathbf{r}')$ is the direct correlation function of Ornstein and Zernike. c_2 , like g , does double duty, expressing both structural and linear response properties, which is why its restriction has such strong implications. The approximation, very much in the Ornstein-Zernike spirit, that c_2 is unchanged from its reference bulk value when nonuniformity is imposed is in a way the prototype of a number of free energy density functional approximations that have been made.⁽⁶⁾ Consistency is now no problem, since iterated application of $\delta/\delta n(r)$ yields the sequence

$$c_s(1, \dots, s) = 0, \quad s > 2 \quad (2.6)$$

for the higher direct correlation functions, which certainly maintains symmetry.

In fact, consistency implies integrability in the sense that a free energy can be constructed to describe the fluid. We start by writing

$$c_2(\mathbf{r}, \mathbf{r}') = c(\mathbf{r} - \mathbf{r}') \quad (2.7)$$

c being our basic model function, then observe that

$$\frac{\delta}{\delta n(\mathbf{r}')} \beta[\mu - u(\mathbf{r})] = \frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})} - c(\mathbf{r} - \mathbf{r}') \quad (2.8)$$

integrates to the profile equation

$$\beta[\mu - u(\mathbf{r})] = \ln n(\mathbf{r}) - \int c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d^3 r' \quad (2.9)$$

which of course implies (2.5). Here μ is the (momentum-reduced) chemical potential. Following this,

$$\delta \beta F^B / \delta n(\mathbf{r}) = \beta[\mu - u(\mathbf{r})] \quad (2.10)$$

integrates to

$$\beta F^B = \int [n(\mathbf{r}) \ln n(\mathbf{r}) - n(\mathbf{r})] d^3 r - \frac{1}{2} \iint n(\mathbf{r}) c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d^3 r d^3 r' \quad (2.11)$$

Here F^B is the bulk or internal Helmholtz free energy, in which the external field energy has been subtracted out,

$$F^B = F - \int n(\mathbf{r}) u(\mathbf{r}) d^3r \quad (2.12)$$

From (2.11), all of thermodynamics can now be constructed.

3. PHASE TRANSITIONS

Of the other free energies obtainable from (2.11), the grand canonical potential

$$\Omega = F^B - \int n(\mathbf{r}) [\mu - u(\mathbf{r})] d^3r \quad (3.1)$$

is particularly useful. Inserting (2.11), we have

$$\beta\Omega = - \int n(\mathbf{r}) d^3r + \frac{1}{2} \iint n(\mathbf{r}) c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d^3r d^3r' \quad (3.2)$$

clearly the prototype of a power series expansion in $n(\mathbf{r})$. Some appreciation for the peculiarities of the model that has now been designed can be gleaned from its restriction to uniform density $n(\mathbf{r}) = n$. Since we can expect $\Omega = -PV$ for a uniform system, (3.2) reduces to $-\beta PV = -nV + (1/2) n^2 V c_0$, where c_0 is the total integral or zeroth moment of c , and hence to the equation of state

$$\beta P = n - \frac{1}{2} c_0 n^2 \quad (3.3)$$

When $c_0 > 0$, the grand canonical manifestation (3.3) is odd indeed. The exaggerated Van der Waals loop has however been recognized⁽⁷⁾ as an artifact due to the divergent fluctuations in particle number at maximum P , so that in fact $\Omega \neq -PV$. By going over to the canonical ensemble obtained from (3.3) via

$$e^{-\beta\Omega} = \Xi = \sum e^{N\beta\mu} Q_N = \sum e^{\beta(N\mu - F_N)} \quad (3.4)$$

matters clarify. In terms of the activity $z = e^{\beta\mu}$, and using (2.9), then (3.4) becomes

$$\sum z^N e^{-\beta F_N} = e^{V[n - (1/2)c_0 n^2]} \quad \text{where} \quad z = n e^{-nc_0} \quad (3.5)$$

giving rise to the large N -asymptotic solution⁽⁸⁾

$$-\beta F_N = \begin{cases} N \left(1 + \frac{1}{2} c_0 \frac{N}{V} - \ln \frac{N}{V} \dots \right), & \frac{N}{V} < \frac{1}{c_0} \\ N \left(1 + \frac{1}{2c_0} \frac{V}{N} + \ln c_0 \dots \right), & \frac{N}{V} > \frac{1}{c_0} \end{cases} \quad (3.6)$$

For the pressure $P = -\partial F/\partial V$, we then have

$$\beta P = \begin{cases} n - \frac{1}{2} c_0 n^2, & n < 1/c_0 \\ 1/(2c_0), & n > 1/c_0 \end{cases} \quad (3.7)$$

a perfectly reasonable flat isotherm, leading to an infinite density condensed phase.

We surmise that a spatial separation into these two phases will not occur in the grand canonical ensemble, e.g., the Helmholtz free energy (2.11) gives rise only to the first of (3.6). However, in conformity with the peculiar nature of the system, there does exist a spatial transition from the $n = 1/c_0$ transition fluid to $n = 0$ vapor! This anomalous state is supported on the $n = 0$ side by a nonvanishing logarithmic density gradient, so that the bulk pressure of zero is not relevant. To illustrate the phenomenon, suppose that

$$c(\mathbf{r}) = c_0 \frac{\lambda^2}{4\pi} \frac{e^{-\lambda r}}{r} \quad (3.8)$$

so that

$$\frac{1}{c_0} \left(1 - \frac{1}{\lambda^2} \nabla^2 \right) c(\mathbf{r}) = \delta(\mathbf{r}) \quad (3.9)$$

Then from (2.9) we have in the absence of external field

$$\frac{\beta\mu}{c_0} = \frac{1}{c_0} \left(1 - \frac{1}{\lambda^2} \nabla^2 \right) \ln n(\mathbf{r}) - n(\mathbf{r}) \quad (3.10)$$

Writing

$$n(\mathbf{r}) = \frac{1}{c_0} e^{w(\mathbf{r})} \quad (3.11)$$

and recalling from (3.5) that $e^{\beta\mu} = 1/(c_0 e)$ at the transition vapor density $n = 1/c_0$, (3.10) becomes

$$\frac{1}{\lambda^2} \nabla^2 w(\mathbf{r}) + e^{w(\mathbf{r})} - 1 - w(\mathbf{r}) = 0 \quad (3.12)$$

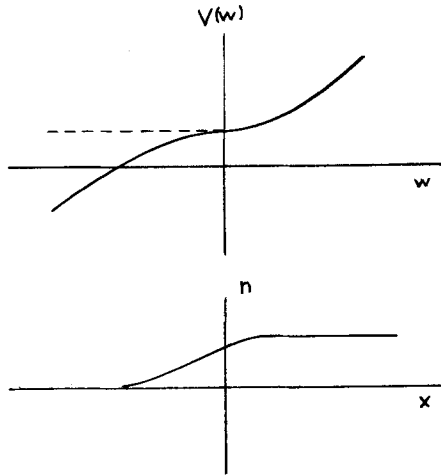


Fig. 1. Interface potential $V(w)$ and density profile $n(x)$.

If the density is stratified in the x direction, (3.12) has the energy integral

$$\frac{1}{\lambda^2} w'(x)^2 + V(w(x)) = 1 \tag{3.13}$$

$$V(w) = e^w - w - \frac{1}{2}w^2$$

where the energy constant is determined by the asymptotic condition that $w = 0$ when $w'(x) = 0$. The trajectory in w space is seen to be from $w = -\infty$ to $w = 0$, at which point $V'(w) = 0$. To estimate the profile, we observe that near $w = 0$,

$$\frac{1}{\lambda^2} w'(x)^2 + \frac{1}{2} w(x)^3 = 0 \tag{3.14}$$

so that, e.g.,

$$w(x) = -\frac{24}{\lambda^2} \frac{1}{x^2} \tag{3.15}$$

yielding the claimed transition from $n = 0$ to $n = 1/c_0$, with $1/e$ value at $x = (24)^{1/2}/\lambda$. This is not accurate on the tail at large $-w$, where $w'/(\frac{1}{2}w^2 + w + 1)^{1/2} = \lambda$ yields instead

$$w(x) + 1 = \sinh(\lambda x / \sqrt{2} + K) \tag{3.16}$$

4. THE MANY-BODY POTENTIALS

The model (2.9) is of course familiar. In the form

$$n(\mathbf{r}) = e^{\beta[\mu - u(\mathbf{r})]} \exp \left[\int c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d^3r' \right] \quad (4.1)$$

it is simply the nonlinear Debye-Hückel equation,⁽⁹⁾ with pair interaction $-\beta\phi$ replaced by c . On the other hand, if the external potential is taken as $\phi(r)$, that due to a particle sitting at the origin, it reads, since then $n(\mathbf{r}) = ng(\mathbf{r})$,

$$\beta\phi(\mathbf{r}) - \beta\mu = -\ln n - \ln g(\mathbf{r}) + n \int c(\mathbf{r} - \mathbf{r}') h(\mathbf{r}') d^3r' + n \int c(\mathbf{r} - \mathbf{r}') d^3r' \quad (4.2)$$

implying both (let $r \rightarrow \infty$)

$$\ln(n/z) = 1 - \partial\beta P/\partial n \quad (4.3)$$

and

$$\beta\phi(\mathbf{r}) + \ln g(\mathbf{r}) = g(\mathbf{r}) - 1 - c(\mathbf{r}) \quad (4.4)$$

The second is the well-known HNC approximation, and the first an equation of state consistent with (3.3).

But is (2.9) a model of anything? Is there some set of internal many-body interactions that gives rise to (3.2)? It is not just a matter of having the right number of functions available for the purpose—there are enough. Rather, the question is whether, e.g., the grand partition function $\Xi = e^{-\beta\Omega}$ results from a nonnegative probability kernel, or more explicitly whether we can write

$$\Xi = \sum \frac{1}{s!} \int \cdots \int \prod_1^s e(\mathbf{r}_i) \exp[-\beta V_s(\mathbf{r}_1, \dots, \mathbf{r}_s)] d^3r_1 \cdots d^3r_s \quad (4.5)$$

where $e(\mathbf{r}) = e^{\beta[\mu - u(\mathbf{r})]}$, for a suitable set V_s . To this end, we need only eliminate $n(\mathbf{r})$ from (3.2) and (4.1), written as

$$\Xi = \exp \left[\int n(\mathbf{r}) d^3r - \frac{1}{2} \iint n(\mathbf{r}) c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d^3r d^3r' \right] \quad (4.6)$$

where

$$n(\mathbf{r}) = e(\mathbf{r}) \exp \int c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') d^3r' \quad (4.7)$$

and compare with (4.5). A graphical analysis is by far the easiest way to proceed.

To start with, consider (4.7), written in graphical form (filled-in element integrated, open element unintegrated) as shown

$$\square = \sum \frac{1}{s!} \left\{ \begin{array}{c} \blacksquare \\ | \\ \circ \\ / \quad \backslash \\ \blacksquare \quad \blacksquare \\ \quad \quad \quad \vdots \\ \quad \quad \quad \blacksquare \end{array} \right\} s$$

e

or on integrating,

$$n(r) = \sum (\text{labeled } r\text{-rooted trees with nodes } e \text{ and bonds } c) / \text{graph symmetry} \tag{4.8}$$

Rather than inserting this directly into (4.6), it is simpler to first note that since

$$n(r) = -\beta e(r) \frac{\delta \Omega}{\delta e(r)} \tag{4.9}$$

then (4.8) implies at once

$$-\beta \Omega = \sum (\text{labeled unrooted trees}) / \text{graph symmetry}. \tag{4.10}$$

Now we can exponentiate (4.10) to obtain

$$\Xi = \sum (\text{labeled unrooted tree complexes}) / \text{graph symmetry} \tag{4.11}$$

Written out, then

$$\begin{aligned} \Xi = & 1 + \frac{1}{2!} \{ \cdot \quad \cdot + \text{---} \} + \frac{1}{3!} \{ \cdot \quad \cdot + 3 \text{---} + 3 \cdot \quad \cdot \} \\ & + \frac{1}{4!} \{ \cdot \quad \cdot + 6 \text{---} + 3 \text{---} + 12 \text{---} \\ & + 12 \text{---} + 4 \text{---} \} + \dots \end{aligned} \tag{4.12}$$

Hence, comparing with (4.5),

$$\begin{aligned} e^{-\beta V_2(1,2)} &= 1 + c(1, 2) \\ e^{-\beta V_3(1,2,3)} &= 1 + \sum c(i, j) + \sum c(i, j) c(j, k) \\ e^{-\beta V_4(1,2,3,4)} &= 1 + \sum c(i, j) + \sum c(i, j) c(k, l) + \sum c(i, j) c(j, k) \\ &\quad + \sum c(i, j) c(j, k) c(k, l) + \sum c(i, l) c(j, l) c(k, l) \\ &\quad \dots \end{aligned} \tag{4.13}$$

where only distinct terms are included in each sum.

5. REALIZABILITY CONDITIONS

The restrictions on the available model function $c(1, 2)$ are now readily found. Since $\exp[-\beta V_2(1, 2)] \geq 0$, then according to (4.13),

$$c(1, 2) \geq -1 \tag{5.1}$$

Moving to the next step,

$$e^{-\beta V_3(1,2,3)} = e^{-\beta V_2(1,2)} e^{-\beta V_2(1,3)} e^{-\beta V_2(2,3)} \times \left[1 + \frac{c(1, 2)}{1 + c(1, 2)} \frac{c(2, 3)}{1 + c(2, 3)} \frac{c(3, 1)}{1 + c(3, 1)} \right] \tag{5.2}$$

Thus, if geometric relations between 1, 2, and 3 are ignored so that $c(1, 2)$, $c(2, 3)$, $c(3, 1)$ are independent, we require $c(1, 2)/[1 + c(1, 2)] \geq -1$, or

$$c(1, 2) \geq -\frac{1}{2} \tag{5.3}$$

(5.1) and (5.3) suggest decreasing negativity as s in V_s increases. To strengthen this suggestion, consider the s th of (4.13), in which at most $s - 1$ links occur. The product $c(2, s) c(3, s) \cdots c(s - 1, s)$ occurs only in the term $[1 + c(1, 2) + c(1, 3) + \cdots + c(1, s)] c(2, s) c(3, s) \cdots c(s - 1, s)$. Hence, if as in (3.8) the $c(i, j)$ can be arbitrarily large, the limit

$$\lim_{\substack{c(2,s) \rightarrow \infty \\ \dots \\ c(s-1,s) \rightarrow \infty}} \frac{e^{-\beta B_s}}{c(2, s) \cdots c(s - 1, s)} = 1 + c(1, 2) + \cdots + c(1, s) \tag{5.4}$$

together with the same independence assumption as above, shows that $c(12) \geq -1/(s - 1)$, or going to arbitrarily large s , that

$$c(1, 2) \geq 0 \tag{5.5}$$

The condition (5.5) is also sufficient for the sequence of many-body potentials V_s to exist, since the right-hand side of (4.13) is now guaranteed to be nonnegative. It is of course not sufficient for the convergence of the grand ensemble thermodynamic functions, but this presumably has a direct physical basis: the convexity of the free energy, and hence the stability of the system, is equivalent to the restriction

$$\frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})} - c(\mathbf{r} - \mathbf{r}') \text{ is positive semidefinite} \tag{5.6}$$

which must thereby be enforced. Its failure in the uniform case for $n > 1/c_0$

was precisely the reason for the analysis (3.4)–(3.7). However, if (5.5) holds, $\{c(\mathbf{r} - \mathbf{r}')\}$ has c_0 as its largest eigenvalue, so that (5.6) is necessarily valid when $n(r) \geq 1/c_0$ pointwise.

6. CONCLUSION

We have constructed a set of solvable classical fluids with special many-body interactions, but arbitrary external field. The “net interaction,” according to (5.5), is restricted to be attractive, permitting the occurrence of a phase transition in a canonical ensemble, but producing an infinite density condensed phase. Reduction to a canonical ensemble for the non-uniform fluid seems notably nontrivial. Nonetheless, in addition to the obvious possibility of using such systems out of their domain of microscopic validity, they may serve as useful references to which repulsive potentials can be applied, e.g., perturbatively. It is also true that extension of (3.2) to higher-order polynomials, to generalized rational fractions, and for that matter to the use of dimensionless pair functions other than $c(1, 2)$, are strongly suggested, but these must remain tasks for the future.

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