Quasi-one dimensional classical fluids*

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We study the equilibrium statistical mechanics of simple fluids in narrow pores. A systematic expansion is made about a one-dimensional limit of this system. It starts with a density functional, constructed from projected densities, which depends upon projected one and two-body potentials. The nature of higher order corrections is discussed.

Key words: classical fluids, one-dimensional limit, narrow pores, higher order corrections

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1. Introduction

The physical sciences are all about constructing models of reality, and Myroslav Holovko is one of the expert practitioners of the art [1]. The model may be very close to reality, so that needed corrections are readily applied, but then the model itself may be hard to analyze. Or it may be very primitive and easily solved in detail, in which case everything depends upon systematic, perhaps ingenious, correction procedures. Fortunately, there are numerous situations that allow the advantages of both extremes to be combined. One of these, that of molecular systems under molecule-scale confinement, is assuming an increasing importance as nanoscale control promises to approach the routine. In this brief communication, we would like to address a subcategory of this impressive array that ranges from fluids in biological pores [2] to those in industrial zeolites.

A traditional activity in theoretical chemical physics is that of deriving the properties of bulk fluids in thermal equilibrium. When surfaces abound, imposed or self-generated, naive thermodynamic approaches fail in detail, even with simple fluids, and more powerful techniques are required. Well-established integral equation methods [4] have no difficulty in principle in dealing with these systems, but they become quite cumbersome. Density functional approaches [5] – often much more of an art than a science – while fairly ancient in both classical and quantum versions, have

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more and more filled in this area. Their aim has generally been to emphasize structural accuracy of the model employed, rather than to develop effective correction procedures, and almost all rely conceptually upon piecing together suitably localized bulk fluids. When the model system is sufficiently specialized, e.g. classical pure hard cores in equilibrium, impressive accuracy is obtained, as in Rosenfeld’s extension [6] of the structure suggested by Percus [7]. But when 3-dimensional bulk provides a poor picture of a system at all levels of resolution, one can do better. Here, as mentioned, we will deal with classical fluids confined to a pore-like space, so that they are best termed quasi-one-dimensional, and literal one-dimensional space becomes the conceptual reference. Indeed, as we will show, it is more than just conceptual.

2. The one-dimensional fluid

The term quasi-one-dimensional loses its vagueness when confinement is so tight that the particles involved must maintain their order, i.e. they cannot pass each other, and so remain in single file. And for sufficiently tight confinement, if the interparticle forces have a small enough range in comparison with that of the assumed hard core, this is equivalent to having only next neighbor interactions. Under these circumstances, one can imagine the limiting model of next-neighbor interacting particles in a common one-dimensional space. If one wants to allow for an arbitrary external potential and arbitrary interactions – restricted as above – this is not a trivial situation to analyze, but it can be done. In the one species case, it requires the introduction of a single auxiliary field \( \Lambda(x) \) to accompany the observable particle density field \( u(x) \), and results [8] in the (1-D) grand ensemble excess Helmholtz free energy – at reciprocal temperature \( \beta \) – concisely written as

\[
\beta F_{1}^{\text{ex}}[n, \Lambda, w] = \int n \ln(1 + w \Lambda) - \int (n \ln n - n) - \ln(1 + \int \Lambda). \tag{2.1}
\]

Here \( w(x, x') = e^{-\beta \phi(x'-x)}\theta(x'-x) \) is the one-sided next neighbor interaction Boltzmann factor, and in \( (w\Lambda)(x) = \int w(x, x') \Lambda(x') dx' \), it acts as an integral operator. The local chemical potential \( \mu(x) = \mu - u(x) \) for external potential \( u(x) \) is then obtained as usual:

\[
\text{if} \quad \beta \mu(x) = \ln n(x) + \beta \mu^{\text{ex}}(x),
\]

\[
\text{then} \quad \beta \mu^{\text{ex}}(x) = \delta \beta F^{\text{ex}}/\delta n(x)|_{\Lambda} = \ln(\Lambda(x)/n(x)) - \ln(1 + (w\Lambda)(x)), \tag{2.2}
\]

and the implied condition on (2.1) that \( \beta F^{\text{ex}} \) is stationary with respect to \( \Lambda \) yields

\[
0 = \delta \beta F^{\text{ex}}/\delta \Lambda(x)|_{n} = \frac{n(x)}{\Lambda(x)} - \left( w^{T} \frac{n}{1 + w\Lambda} \right)(x) - \frac{1}{1 + \int \Lambda(x') dx'}, \tag{2.3}
\]

here \( w^{T} \) is the transpose of \( w \).

In the special case of hard rods of diameter \( a \), \( \Lambda \) can be eliminated from (2.1) via (2.3), resulting in

\[
\beta F^{\text{ex}} = \int n_{\sigma}(x) \ln(1 - an_{\sigma}(x)) dx, \tag{2.4}
\]
where
\[ n_\sigma(x) = \frac{1}{2}(n(x + a/2) + n(x - a/2)), \quad n_\tau(x) = \frac{1}{a} \int_{-a/2}^{a/2} n(x + x') dx'. \]

(which generalizes without difficulty to hard core mixtures as well). The fact that (2.4) represents a local free energy density that is a function of only the linearly weighted densities \( n_\sigma(x) \) and \( n_\tau(x) \), results in a uniform fluid direct correlation function which is bilinear on a vector space of only two dimensions as the bulk density varies. Since the bulk direct correlation function for a PY-approximated hard sphere fluid can similarly be constructed from a vector space of dimension five [7], this suggests that its non-uniform generalization be constructed from the corresponding weighted average densities, which is the genesis [9] of the Rosenfeld approach, among others. We will be interested in seeing whether such a structure persists under tight confinement.

3. Quasi-one dimensional expansion

In a way, our objective is to look at a pore-confined fluid at low resolution, so that we are projecting onto a one-dimensional fluid, and dimension-reducing projection methods have a long history. But we will want to be very explicit in carrying out this reduction. From a density functional viewpoint, the path is clear: we have a density pattern \( n(x, y) \), where \( x \) denotes longitudinal direction (actually, it need not be a Cartesian axis) and \( y \) encompasses the transverse coordinates. In the situation of interest, we can imagine starting with a basic pattern \( n_0(x, y) \) and then squashing it down transversely to \( n(x, y) \) by contracting the confining space via an external field. The result would then appear as

\[ n(x, y) = n_0(x, y/a)/a^{D-1}, \quad \text{(3.1)} \]

where \( a \) measures the contraction ratio. As \( a \to 0 \), the observed density pattern is strictly one-dimensional (\( D \) denotes the actual spatial dimensionality), conserving, however, the density per unit length

\[ n_0(x) = \int n(x, y) d^{D-1} y = \int n_0(x, y) d^{D-1} y. \quad \text{(3.2)} \]

To make use of (3.1) and (3.2) systematically, one can first write down an explicit expression, e.g. a diagrammatic expansion [10] for

\[ \beta F^{\text{ex}}[n(x, y), f(x, y; x', y')], \]

where \( f = e^{-\beta\phi} - 1 \) is the pair interaction Mayer function, assuming only pair (and singlet) potentials. Then, rewrite this as

\[ \beta F^{\text{ex}}[n_0(x, y/a)/a^{D-1}, f(x, y; x', y')], \]
and finally make the transformation $y \to ay$ in all integrals. The result is clearly that
\[
\beta F^{\text{ex}}[n(x, y), f(x, y; x', y')] = \beta F^{\text{ex}}[n_0(x, y), f(x, ay; x', ay')],
\] (3.3)
which can then be expanded directly in $a$, or to higher accuracy with no additional labor, expanded in the difference
\[
\Delta f(x, ay; x', ay') = f(x, ay; x', ay') - f_0(x; x'),
\] (3.4)
where $f_0(x; x') = f(x, 0; x', 0)$. The leading order in the expansion of (3.3) is at $\Delta f = 0$, i.e.
\[
\beta F^{\text{ex}}[n(x, y), f(x, y; x', y')] = \beta F^{\text{ex}}[n_0(x, y), f_0(x; x')] + \cdots,
\]
which, transforming back, is just $\beta F^{\text{ex}}[n(x, y), f_0(x, x')] + \cdots$. But the $y$ integrations can then be done at once, requiring only $\int n(x, y) d^{D-1}y = n_0(x)$. We conclude that the leading order is given by
\[
\beta F^{\text{ex}}[n, f]|_{f=f_0} = \beta F^{\text{ex}}_1[n_0, f_0],
\] (3.5)
the strictly one-dimensional free energy in which only the full projected density and the interaction at $y = y' = 0$ appears: the obvious projection is correct at this order. The interest, of course, is in what happens at higher order.

The diagrammatic background in which (3.5) was derived is crucial, but details are not necessary until one tries to be explicit. So we can start a full expansion by just carrying out a formal Taylor expansion with respect to $f$ around $f_0$:
\[
\beta F^{\text{ex}}[n, f] = \sum_{s=0}^\infty \frac{1}{s!} \int \cdots \int \frac{\delta^s \beta F^{\text{ex}}[n, f]}{\delta f(x_1, y_1; x'_1, y'_1) \cdots \delta f(x_s, y_s; x'_s, y'_s)}|_{f=f_0}
\times \prod_{j=1}^s \Delta f(x_j, y_j; x'_j, y'_j) \prod_{j=1}^s (dx_j dx'_j d^{D-1}y_j d^{D-1}y'_j).
\] (3.6)

The zeroth order term is known from (3.5), but the first order term is already significant: the combination
\[
\Delta f(x, y; x', y')/\delta f(x, y; x', y')|_{f=f_0}
\]
clearly replaces all $f$-bonds but one in $\beta F^{\text{ex}}$ by $f_0$ and converts that one to $\Delta f(x, y; x', y')$; the $y$ integrations other than $d^{D-1}y d^{D-1}y'$ then replace all $n$’s by $n_0$’s except for $n(x, y)$ and $n(x', y')$. But let us set
\[
n(x, y) = n_0(x) \rho(x, y)
\] (3.7)
and similarly, of course, for $n(x', y')$. Then all nodes are $n_0$’s, all $f$’s but one are $f_0$’s and that one becomes, on $y, y'$ integration
\[
\Delta f_0(x, x') = \iint \rho(x, y) \Delta f(x, y; x', y') \rho(x', y') d^{D-1}y d^{D-1}y'.
\] (3.8)
Only the $x$-integrations remain, and we conclude that
\[
\left( \iint \Delta f(x, y; x', y') \frac{\delta}{\delta f(x, y; x', y')} \, dx \, dy \right) F_{\text{ex}}^n[f, f]_{f = f_0} =
= \left( \iint \Delta f_0(x, x') \frac{\delta}{\delta f_0(x, x')} \, dx \, dx' \right) F_{\text{ex}}^n[n_0, f_0].
\] (3.9)

If equation (3.9) were to apply to products of Taylor operators as well, we would conclude that
\[
F_{\text{ex}}^n[n, f] = F_{\text{ex}}^n[n_0, f_0 + \Delta f_0] = F_{\text{ex}}^n[n_0, \tilde{f}_0],
\] (3.10)
where
\[
n_0(x) = \int n(x, y) \, dy
\]
and
\[
\tilde{f}_0(x, x') = \iint \rho(x, y) f(x, y; x', y') \rho(x', y') \, dx \, dy
\]
and it is indeed this first approximation that we will examine in detail. One should note of course that the same result would be obtained by expanding about an unknown $f_0(x, x')$ rather than $f_0(x, x')$ and requiring the first correction to vanish.

4. Application

To make use of (3.10), we need the strictly one-dimensional solution, with interaction Boltzmann factor
\[
w_0(x, x') = (1 + \tilde{f}_0(x, x')) \theta(x' - x).
\] (4.1)
Since (4.1) has in general no special properties aside from those emanating from the short range of $f_0$, we have little choice but to avail ourselves of the exact equation (2.1), reading here
\[
\beta F_{\text{ex}}^n[n, \Lambda] = \int n_0(x) \ln \frac{\Lambda(x)}{1 + \int_x^{\infty} (1 + f_0(x, x')) \Lambda(x') \, dx'} \, dx
- \int (n(x) \ln n(x) - n(x)) \, dx - \ln(1 + \int_{-\infty}^{+\infty} \Lambda(x') \, dx'),
\] (4.2)
where
\[
\delta \beta F_{\text{ex}}^n / \delta \Lambda(x) = 0.
\]
The complicating factor is the necessity of solving for $\Lambda(x)$ to insert into $\beta F_{\text{ex}}^n$. But since (4.2) is stationary in $\Lambda$, a viable option is to simply insert a reasonable ansatz for $\Lambda$, such as its form when $\tilde{f}_0(x, x')$ is taken simply as $f_0(x, x') = f(x, 0; x', 0)$, and this form is indeed known in the hard core case. Results along these lines will be reported elsewhere.
If our standards are lowered a bit, we may be content with the first order correction arising from (3.9). Then, the required input information is only that obtained from the strictly 1-D Mayer factor. Let us see how this goes. What we need specifically is \( \delta \beta F_1^{\text{ex}}[n_0, f_0]/\delta f_0(x, x') \), but since \( \beta F_1^{\text{ex}} \) is stationary with respect to \( \Lambda \), we can just differentiate (2.1) at constant \( \Lambda \), resulting at once in

\[
\delta \beta F_1^{\text{ex}}[n_0, f_0]/\delta f_0(x, x') = -\frac{n_0(x)\Lambda_0(x')\theta(x' - x)}{1 + (w_0\Lambda_0)(x)}.
\]

Here our first order expansion becomes the very accessible

\[
\beta F_0^{\text{ex}}[n, f] = \beta F_1^{\text{ex}}[n_0, f_0] - \iint_{x' \geq x} \frac{n_0(x)}{1 + (w_0\Lambda_0)(x)} \Delta f_0(x, x')\Lambda_0(x')dx'dx'.
\]

For hard spheres, where the one-dimensional reference is that of hard rods, \( \Lambda_0 \) is indeed known, and so (4.4) is completely explicit. An immediate consequence, incidentally, is that there will be no \( F_1^{\text{ex}} \) local density that is a function only of finitely many weighted densities.

5. Higher corrections

To see why approximation (3.10) is incomplete, one can develop the higher derivative extensions of (3.9). It’s simplest to go directly to the standard Mayer expansion of the excess free energy \( F_1^{\text{ex}}[n, f] \). In this form, one has a weighted sum of integrated diagrams, each of which consists of nodes \( n(x, y) \) joined by bonds \( f(x, y; x', y') \). Thus, \( F_0^{\text{ex}}[n, f_0 + \Delta f] \) will consist of the same diagrams with \( f_0(x, x') \) bonds, a certain subset of which has been replaced by \( \Delta f(x, y; x', y') \) bonds. These subsets can be decomposed into connected subsets joined to the rest of the diagrams by \( f_0 \) bonds. One can now set \( n(x, y) = n_0(x)\rho(x, y) \), as in (3.7), and carry out all \( y \)-integrations. Any node not belonging to a \( \Delta f \)-bond will, since \( \int \rho(x, y)d^{D-1}y = 1 \), reduce to \( n_0 \). A connected \( \Delta f \) subset will, however, integrate to an entangled object which, if comprising \( \gamma \) nodes, will be recognized as the Mayer \( f \)-function of a \( \gamma \)-particle interaction. In order of complexity, there will be 2-particle factors, 3-particle factors, \( \cdots \):

\[
\Delta f_2(x, x') = \iint \rho(x, y)\Delta f(x, y; x', y')\rho(x', y')d^{D-1}yd^{D-1}y',
\]

\[
\Delta f_3(x, x', x'') = \iiint \rho(x, y)\Delta f(x, y; x', y')\rho(x', y')
\times \Delta f(x', y'; x'', y'')\rho(x'', y'')d^{D-1}yd^{D-1}y'd^{D-1}y'',
\]

\[
\Delta f_3'(x, x', x'') = \iiint \rho(x, y)\Delta f(x, y; x', y')\rho(x', y')
\times \Delta f(x', y'; x'', y'')\rho(x'', y'')\Delta f(x'', y''; x, y)d^{D-1}yd^{D-1}y'd^{D-1}y'',
\]

\[
\cdots
\]

and systematizing these contributions is not difficult. Let us just start the process.

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One wants to compare the one-dimensional free energy expansion generated by the sequence (5.1) with what would have been obtained for a system governed by a sequence of 2-body, 3-body, \cdots interactions. In the latter case, the Mayer expansion would be that of $\Pi(1 + f_{ij})\Pi(1 + f_{ijk})\cdots$, and the next correction we would want corresponds to the 3-body cluster that would appear in the form $(1 + f_{ij})(1 + f_{jk})(1 + f_{ik})f_{ijk}$. Thus, adding up the 4 connected 3-body terms of (5.1), we have in effect appended a 3-particle interaction with $f$-function

$$f_3(x, x', x'') = \left[ \int \int \int \rho(x, y)(1 + \Delta f(x, y; x', y'))\rho(x', y') (1 + \Delta f(x', y'; x'', y'')) \right.$$

$$\times \rho(x'', y'')(1 + \Delta f(x'', y''; x, y))d^{D-1}y d^{D-1}y' d^{D-1}y'' - 1$$

$$\left. \times [(1 + \bar{f}_0(x, x'))(1 + \bar{f}_0(x', x''))(1 + \bar{f}_0(x'', x))]^{-1} \right] .$$

(5.2)

Actually, complexity only arises as one departs further and further from the nearly one-dimensional domain that we are interested in. For example, if $\Delta f(x, y; x', y')$ vanishes (for accessible $y$ and $y'$) except in a narrow range of $|x - x'|$, as would be the case for hard objects with small limited transverse motion, there will be no contribution from any subdiagram with loops. The remaining tree diagrams can be handled by more routine methods.

6. Conclusion

We conclude that in our chosen arena, effective systematic methods exist for carrying out the low resolution reduction that is perhaps the qualitative objective of any quantitative theory. The general strategy is quite simple, and extensions are being carried out; that to equilibrium mixtures is direct, as is extension to curved pores, but the time-dependant situation much less so. To be sure, as we depart more and more from one-dimensional reference, the “correction terms” must dominate, and this particular path is not appropriate. However, along the way, we expect to find the corrections come in one bunch at a time, as it becomes necessary to track larger and larger sets in what started out as strictly single file (see [8] for a discussion of the beginning of the sequence, in a somewhat different context). In other words, each bunch signals an analytic break – but weaker and weaker – in the thermodynamic behavior. Whether or not the increased complexity merits a detailed study is not obvious, but such an investigation is indeed under way.

References


Квазіодновимірні класичні пліни

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Ми вивчаємо рівноважну статистичну механіку простого пліну в обмежених порах. Систематичне розглядення виконане в однорідній гранції цієї системи, яка базується на функціоналі густини, по-будованому з проектованих густин, що залежать від одно- і двочастинкових потенціалів. Обговорюється природа кореляцій вищих порядків.

Ключові слова: класичні пліни, однорідна граніця, обмежені пори, кореляції вищих порядків

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