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Asymptotic Density Profile of a Classical Fluid Against a Hard Wall

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The asymptotic density profile of classical simple fluids in contact with a hard wall is studied using the hypernetted chain approximation for inhomogeneous systems. It is shown that the one-particle distribution function tends very slowly to the density of the bulk, also in absence of a long-range wall–particle interaction, when the pair interaction between particles in the bulk varies as an inverse power at large distances.

KEY WORDS: Density profile; correlations; inhomogeneous fluids; hard wall; gradient expansion; Coulomb liquids.

1. INTRODUCTION

The asymptotic behavior of the correlation functions of homogeneous fluids near the triple point has been extensively investigated in the literature.[1–4] So far much less information is available in the case of inhomogeneous fluids.

In this paper we investigate the asymptotic behavior of the density profile $\rho(z)$ of a classical simple fluid against a hard wall using the hypernetted chain approximation (HNC). Notwithstanding the absence of a long-range interaction between the wall and the particles, the density profile of an inverse-power-law fluid tends very slowly to the density of the bulk.

In Section 2 we derive the HNC results for the asymptotic density profile in the case of inverse power fluids; in Section 3 we show the modifications necessary to deal with the long-range Coulomb potential and comparison is made with the gradient expansion approach.

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2. INVERSE POWER FLUIDS

The HNC equation for the one-particle density $\rho(z)$ of a fluid against a hard wall without wall–particle interaction is[5]

$$\log \frac{\rho(z)}{\rho_b} = \rho_b \int d\mathbf{r}' \, c_b(|\mathbf{r}-\mathbf{r}'|) \, h(z') \tag{1}$$

where z is the vertical distance from the surface, ρ_b is the bulk density, $h(z) = [\rho(z) - \rho_b]/\rho_b$, $c_b(r)$ is the direct correlation function of the homogeneous fluid and the integration is over the whole space.

We assume that, for classical liquids where the long-range interaction may be written as $u(r) \sim A/r^n$, the direct correlation function $c_b(r)$ tends asymptotically to $-\beta A/r^n$ plus faster decaying terms ($\beta = 1/kT$). Note that this is an exact statement in the HNC theory of the bulk.

Let us consider a z so large that $z/2$ is also well inside the asymptotic region both for $h(z)$ and $c_b(z)$.

Using cylindrical coordinates Eq. (1) can be written

$$\begin{aligned}
\log[1+h(z)]
&= -2\pi\rho_b \int_{-\infty}^{0} dz' \int_{z-z'}^{\infty} s c_b(s)\, ds + 2\pi\rho_b \int_0^{z/2} dz'\, h(z') \int_{z-z'}^{\infty} s c_b(s)\, ds \\
&\quad + 2\pi\rho_b \int_{z/2}^{z} dz'\, h(z') \int_{z-z'}^{\infty} s c_b(s)\, ds + 2\pi\rho_b \int_z^{\infty} dz'\, h(z') \int_{z-z'}^{\infty} s c_b(s)\, ds
\end{aligned} \tag{2}$$

where we have used the hard wall condition

$$h(z) = -1 \qquad \text{for} \quad z < 0$$

Every term on the right-hand side of Eq. (2) contains either $h(z)$ or $c_b(s)$ integrated in the asymptotic region. Substituting $-\beta A/s^n$ for $c_b(s)$ where $s > z/2$ we get

$$\begin{aligned}
\log[1+h(z)] &\simeq \frac{2\pi\beta A\rho_b}{(n-2)(n-3)\, z^{n-3}} + \frac{2\pi\beta A\rho_b}{(n-2)} \int_0^{z/2} \frac{dz'\, h(z')}{(z-z')^{n-2}} \\
&\quad + 2\pi\rho_b \int_0^{z/2} s c_b(s)\, ds \int_{z-s}^{z+s} dz'\, h(z') \\
&\quad - 2\pi\beta A\rho_b \int_{z/2}^{\infty} \frac{ds}{s^{n-1}} \int_{z/2}^{z+s} dz'\, h(z')
\end{aligned} \tag{3}$$

Furthermore, in the asymptotic region $\log[1+h(z)] \simeq h(z)$ so the density profile should decay as $1/z^{n-3}$ unless one of the remaining integrals on the right-hand side of (3) suppresses this behavior.

We can exclude this case under the very weak assumption that M/z^{ε} would be an upper bound for $|h(z)|$ for $z>0$ ($M>0$; $0<\varepsilon<1$). Indeed

$$\left| \int_0^{z/2} \frac{dz'\, h(z')}{(z-z')^{n-2}} \right| \leqslant M \int_0^{z/2} \frac{dz'}{z'^{\varepsilon}(z-z')^{n-2}} \simeq \frac{M'}{z^{n-3+\varepsilon}} \tag{4}$$

and this term goes to zero faster than the $1/z^{n-3}$ term.

The asymptotic behavior of the remaining two integrals depends on that of $h(z)$ and Eq. (3) must be satisfied in a consistent way. While it is not possible to do this with an exponential decaying density profile, if we put

$$h(z) = -\frac{H}{z^m} + o\left(\frac{1}{z^m}\right) \qquad (m \geqslant n-3)$$

we have at the lowest order

$$\frac{H}{z^m} = \frac{2\pi\beta A\rho_b}{(n-2)(n-3)} \frac{1}{z^{n-3}} + \frac{4\pi\rho_b H}{z^m} \int_0^{\infty} s^2 c_b(s)\, ds + o\left(\frac{1}{z^{n-3}}\right) \tag{5}$$

which requires

$$m = n-3 \qquad \text{and} \qquad H = \frac{2\pi A\rho_b^2 \chi_T}{(n-2)(n-3)}$$

where χ_T is the isothermal compressibility and we have used the Ornstein–Zernike relation: $1-\rho_b \int d\mathbf{r}\, c_b(r) = \beta/\rho_b\chi_T$.

For the physically relevant case of a Lennard-Jones fluid Eq. (5) implies that the density profile tends to the bulk value as slowly as $1/z^3$. We also note that for $n<4$ the adsorption per unit surface area $\int_0^{\infty} h(z)\, dz$ diverges.

The asymptotic behavior of the wall–particle direct correlation function $c(z)$ defined by the relation

$$h(z) = c(z) + \rho_b \int c_b(|\mathbf{r}-\mathbf{r}'|)\, h(z')\, d\mathbf{r}' \tag{6}$$

can be obtained at once using the formula (1) and expanding the $\log(1+h)$. It follows that

$$c(z) = h^2(z)/2 + O(h^3) \tag{7}$$

i.e., in the present case $c(z) = H^2/(2z^{2(n-3)})$ + higher-order terms.

3. COULOMB INTERACTION

In this section we extend the previous analysis to the case in which, in addition to an inverse power potential A/r^n ($n > 3$), we have the Coulomb pair interaction q^2/r. Of course the system will be stabilized by a uniform background of opposite charge.

Equation (1) can be rewritten as

$$\log[1 + h(z)] = -\beta q \varphi(z) + \rho_b \int d\mathbf{r}'\, h(z')\, c_b^R(|\mathbf{r} - \mathbf{r}'|) \tag{8}$$

where $\varphi(z)$ is the electrostatic potential due to the total charge and $c_b^R(r) = c_b(r) + \beta q^2/r$.

For $r \to \infty$, $c^R(r) \to -\beta A/r^n$ and the difference from the previous case in in the $\varphi(z)$ term.

The Poisson equation gives

$$\varphi(z) = 4\pi q \rho_b \int_z^\infty (z - z')\, h(z')\, dz' \tag{9}$$

and the same analysis as in Section 2 shows how the consistency relation (5) is modified by the presence of the Coulomb interaction

$$\frac{4\pi q \rho_b H}{(m-1)(m-2)} \frac{1}{z^{m-2}} = \frac{2\pi \beta A \rho_b}{(n-2)(n-3)} \frac{1}{z^{n-3}} + o\left(\frac{1}{z^{n-3}}\right) \tag{10}$$

whence

$$m = n - 1 \qquad \text{and} \qquad H = \frac{1}{2} \frac{\beta A}{q}$$

Therefore, the presence of the long-range Coulomb interaction speeds up the decay of $h(z)$ the physical reason being in the lowering of the free energy cost of a slower behavior.

As particular case, if the non-Coulombic part of the potential goes to zero faster than any inverse power [*a fortiori* if it is zero as in the case of the one-component classical plasma (OCP)], then relation (8) shows that $h(z)$ must decay faster than any inverse power. Hence in the case of the OCP we get a result which is consistent with that from the gradient expansion.[6]

It is easy to show that the gradient expansion result may be derived from the HNC equation by locally expanding $h(z)$ in a Taylor series[7]: the result is meaningful only as long $c_b^R(r)$ is a short-range function.

The result (6) of the previous section for the wall–particle direct correlation function gives $c(z) = H^2/(2z^{2(n-1)})$ + higher-order terms.

4. CONCLUSIONS

We have found that if the interparticle potential goes as A/r^n for large r, $h(z)$ decays as H/z^{n-3} with H proportional to the isothermal compressibility of the bulk. If also the Coulomb potential is present then $h(z) \sim H/z^{n-1}$. In the case of OCP $h(z)$ must go to zero at least exponentially.

Our analysis of the asymptotic one-particle correlation functions is exact in the HNC approximation. Exact information on the behavior of the corrections to the HNC equation is lacking but it seems reasonable that, in analogy with the known evidence in the homogeneous situation, the correcting terms will decay faster than $h(z)$ not affecting the leading asymptotic behavior of the density profile. A similar statement on the wall–particle direct correlation function requires a stronger assumption on the decaying rate of these unknown corrections.

Although our results are derived for a monocomponent fluid confined by a hard wall, the functional form of the asymptotic density profile does not depend on the exact wall–particle interaction provided it is sufficiently short range, and hence the result should be valid also for soft walls.

Returning in conclusion to the comparison with the gradient expansion, we note that it is not expected to work very well in problems with a hard wall but it should be suitable in the asymptotic region of the density profile.[8] In the case of the OCP the two theories give the same result. It turns out that the gradient expansion gives an exponential decay for any interparticle potential but we expect the HNC result to be more reliable because it takes into account the nonlocal effects of correlations.

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