Solution of Percus's equation for the density of hard rods in an external field

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The theory of a one-dimensional fluid of hard rods has received much attention because it often yields exact results which serve as a guide to understanding the properties of more complicated fluids. Of particular interest recently has been the density distribution of nonuniform fluids in external potentials or between solid walls. The purpose of this paper is to report an explicit solution of the nonlinear integral equation derived by Percus for the density distribution of hard rods.

From the work of Percus[1] and the later work of others,[2,3] it follows that the equilibrium density $n(x)$ of hard rods in an external potential $u(x)$ obeys the nonlinear integral equation

$$\beta\mu=\beta u(x)+\ln n(x)-\ln\left[1-\int_x^{x+\sigma}n(x')dx'\right]+\int_{x-\sigma}^{x}\frac{n(x')}{1-\int_{x'}^{x'+\sigma}n(x'')dx''}dx' , \quad (1)$$

where μ is chemical potential (relative to a convenient datum), σ the rod length, $\beta=1/k_BT$, k_B Boltzmann's constant, and T the absolute temperature.

By introduction of the density functional

$$h(x)=\frac{n(x)}{1-\int_x^{x+\sigma}n(x')dx'} , \quad (2)$$

we can transform Eq. (1) to the form

$$h(x)=e^{\beta[\mu-u(x)]}\exp\left[-\int_{x-\sigma}^{x}h(x')dx'\right] , \quad (3)$$

which admits analytical solution for potentials such that

$$\begin{aligned} e^{-\beta u(x)}&=0 , \quad x<0 , \quad x>L \\ &=e^{-\beta\phi(x)} , \quad 0<x<L , \end{aligned} \quad (4)$$

where $\phi(x)$ is continuous and piecewise differentiable. In this case $h(x)=n(x)=0$ for $x<0$ and $x>L$.

Equations (2) and (3) can be differentiated and rearranged to yield

$$h'(x)=-h(x)[\beta\phi'(x)+h(x)-h(x-\sigma)] \quad (5)$$

and

$$l'(x)=h(x)l(x)-l(x+\sigma)h(x+\sigma) , \quad (6)$$

where $l(x)=n(x)/h(x)$. Equation (4) implies the boundary conditions

$$h(0)=e^{\beta[\mu-\phi(0)]} , \quad n(L)=h(L) \text{ or } l(L)=1 . \quad (7)$$

Thus, we can find $h(x)$ by solving a nonlinear first-order equation and then obtain $n(x)$ as the solution of a linear first-order equation.

The formal solutions to Eqs. (5) and (6) are

$$h(x)=\frac{\exp\left[-\beta\phi(x)+\int_{x_0}^{x}h(x'-\sigma)dx'\right]}{[e^{-\beta\phi(x_0)}/h(x_0)]+\int_{x_0}^{x}\exp\left[-\beta\phi(x'')+\int_{x_0}^{x''}h(x'-\sigma)dx'\right]dx''} \quad (8)$$

and

$$l(x)=l(x_0)\exp\left[\int_{x_0}^{x}h(x')dx'\right]-\int_{x_0}^{x}\exp\left[-\int_{x}^{x''}h(x')dx'\right]l(x''+\sigma)h(x''+\sigma)dx'' . \quad (9)$$

Beginning at $x=0$, Eq. (8) can be solved in the successive intervals $j\sigma<x<(j+1)\sigma$, $j=0,1,2,\ldots$. In the interval $0<x<\sigma$, we obtain

$$h_0(x)=\frac{e^{-\beta\phi(x)}}{e^{-\beta\mu}+\int_0^x e^{-\beta\phi(x')}dx'} . \quad (10)$$

Then

$$h_j(x)=\frac{\exp\left[-\beta\phi(x)+\int_{j\sigma}^{x}h_{j-1}(x'-\sigma)dx'\right]}{[e^{-\beta\phi(j\sigma)}/h_{j-1}(j\sigma)]+\int_{j\sigma}^{x}\exp\left[-\beta\phi(x'')+\int_{j\sigma}^{x''}h_{j-1}(x'-\sigma)dx'\right]dx''} , \quad (11)$$

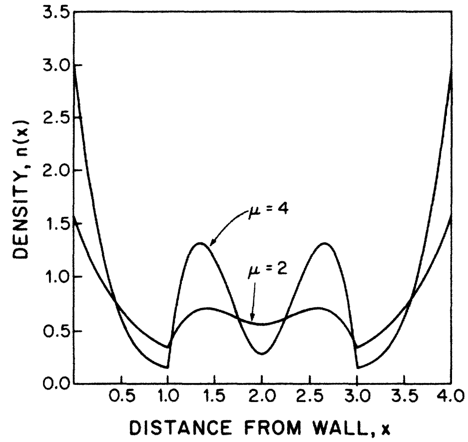

FIG. 1. Density profiles for $L=4\sigma$ and $\beta\mu=2$ and 4.

for $j=1,2,\ldots$. The full solution is thus $h(x)=h_j(x)$, $j\sigma<x<(j+1)\sigma$, $j=0,1,2,\ldots$. When L is not a multiple of σ, then the last interval is $N\sigma<x<L$, where N is the divisor of L with a positive remainder less than σ.

Equation (9) can be solved in the successive intervals $L-(j+1)\sigma<x<L-j\sigma$, $j=0,1,2,\ldots$. The result is

$$l_0(x)=\exp\left[\int_L^x h(x')dx'\right], \quad L-\sigma<x<L \tag{12}$$

$$l_j(x)=l_{j-1}(L-j\sigma)\exp\left[\int_{L-j\sigma}^x h(x')dx'\right] + \int_x^{L-j\sigma}\exp\left[-\int_x^{x''}h(x')dx'\right]l_{j-1}(x''+\sigma) \times h(x''+\sigma)dx'' , \tag{13}$$

$j=1,2,\ldots$. The solution $l(x)$ is then $l(x)=l_j(x)$ $L-(j+1)\sigma<x<L-j\sigma$, $j=0,1,2,\ldots$. The density profile is, of course, given by $n(x)=h(x)l(x)$.

In the case of hard walls, $\phi(x)=0$, Eqs. (10) and (11) yields for $j=0$ the solution

$$h_0(x)=\frac{1}{x+e^{-\beta\mu}} , \tag{14}$$

and for $j\geq 1$

$$h_j(x)=\frac{d}{dx}\ln\left\{1+h_{j-1}(j\sigma)\left[x-j\sigma+h_{j-2}((j-1)\sigma)\left[\frac{(x-j\sigma)^2}{2!}+h_{j-3}((j-2)\sigma)\left[\frac{(x-j\sigma)^3}{3!}+\cdots+h_1(2\sigma)\left[\frac{(x-j\sigma)^{j-1}}{(j-1)!}+h_0(\sigma)\left[\frac{(x-j\sigma)^j}{j!}+\frac{(x-j\sigma)^{j+1}}{(j+1)!}e^{\beta\mu}\right]\right]\cdots\right]\right]\right]\right\} . \tag{15}$$

In particular for $j=1$ and 2,

$$h_1(x)=\frac{d}{dx}\ln\left\{1+h_0(\sigma)\left[x-\sigma+\frac{(x-\sigma)^2}{2}e^{\beta\mu}\right]\right\} \tag{16}$$

and

$$h_2(x)=\frac{d}{dx}\ln\left\{1+h_l(2\sigma)\left[x-2\sigma+h_0(\sigma)\left[\frac{(x-2\sigma)^2}{2}+\frac{(x-2\sigma)^3}{6}e^{\beta\mu}\right]\right]\right\} . \tag{17}$$

Density profiles computed from Eqs. (12)–(15) are plotted in Fig. 1 for $L=4\sigma$ and $\beta\mu=2$ and 4. As expected the density profile is highly structured, with maxima and minima that become more exaggerated with increasing $\beta\mu$. The pressure $[\beta P=n(0)]$, of course, increases monotonically with $\beta\mu$.

Percus has given formulas relating the direct correlation functions of all orders to the density distribution. Thus, the exact solution given here for $n(x)$ provides direct correlation functions. The importance of exactly solvable models is that they provide tests and intuition for the development of approximate theories of more realistic and therefore more complex systems. In a forthcoming publication we explore density profiles and direct correlation functions for several approximate theories that attempt to model real fluids.

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