

Classical fluid in a periodic potential and the density-functional approach

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We investigate the equilibrium state of a one-dimensional fluid of hard-core particles subject to a given external periodic potential. Starting from Percus's exact theory we obtain accurate numerical results for the density profiles and the free energy. These are used for a quantitative test of an approximate free-energy functional frequently used in classical density-functional theories. We show that the density-functional approach works well in a rather broad range of physically interesting parameters. Limits of its applicability are also discussed.

I. INTRODUCTION

The computation of equilibrium properties of nonuniform classical fluids has become a subject of increasing importance for a variety of physical applications, including liquid surfaces,¹ the melting process,² superionic conductors,³ or submonolayer films adsorbed on a crystalline substrate.⁴ The last two examples pose the problem of computing structural and thermodynamic properties of a fluid subject to an external periodic potential. A convenient approach to the general problem is provided by a classical density-functional theory,^{5,6} which yields information on the density $\rho(\mathbf{r})$ and the free energy of the nonuniform state. Other treatments involve the two-particle density $\rho(\mathbf{r}, \mathbf{r}')$ and the Ornstein-Zernike relation. Recent attempts in this direction have been based on the Percus-Yevick approximation,⁷ but are limited so far to one-dimensional systems.

The aim of this paper is twofold. Firstly, we make use of an exact functional relationship, due to Percus,⁸ between an external potential $v(x)$ and the density $\rho(x)$, valid for a one-dimensional system of particles interacting via hard cores. This relationship is evaluated for the case where $v(x)$ is a given periodic potential. An interesting feature of such a system is the interplay between the periodicity of the external potential and the length scale for short-range correlations among the fluid particles, which reflects itself in the detailed behavior of the calculated density distribution.

Secondly, the system described above is treated approximately within a simple version of the density-functional theory. We use a free-energy functional which consists in an expansion up to second order in the density variation about the spatially averaged density $\bar{\rho}$. A functional of this type has been used, for example, in a study of the phase diagram of rare gases adsorbed on graphite⁹ and, more recently, also in connection with the glass transition.¹⁰ A comparison of the method with our accurate results based on the Percus relationship provides a quantitative test of the density-functional approximation (DFA).

It turns out that the DFA works remarkably well in a certain range of parameters, in particular in "incommensurate" situations, where the density variation is reduced in comparison with the case of noninteracting particles. It fails, however, in cases where the particles are substantially localized about the potential minima.¹¹

In Sec. II we briefly recall the Percus relationship and discuss some special cases, part of which are solved analytically. The application of the density-functional theory to our problem is outlined in Sec. III. Finally, in Sec. IV we discuss our numerical results.

II. PERCUS RELATIONSHIP

Percus⁸ has derived an exact relationship between an external potential $v(x)$ and the induced density $\rho(x)$ in a one-dimensional fluid of particles interacting via hard cores,

$$\beta v(x) + \frac{\ln \rho(x)}{z} = \ln \left[1 - \int_{x-a}^x dy \rho(y) \right] - \int_x^{x+a} dy \frac{\rho(y)}{1 - \int_{y-a}^y dw \rho(w)}. \quad (2.1)$$

In this relation a denotes the hard-core diameter, β the reciprocal temperature, and z the fugacity. Furthermore, the grand free energy satisfies⁸

$$\Omega = -\beta^{-1} \int_{-\infty}^{\infty} dx \frac{\rho(x-a)}{1 - \int_{x-a}^x dw \rho(w)}. \quad (2.2)$$

Basically, our aim is to calculate the density $\rho(x)$ for a given periodic potential $v(x) = v(x + 2\pi/k)$ with spatial average \bar{v} . This means that we have to invert Eq. (2.1). It is convenient to write $\rho(x) = \rho_0 + \Delta\rho(x)$, where ρ_0 is the density in the uniform case with $v(x) \equiv \bar{v}$. From Eq. (2.1),

$$\rho_0 = z e^{-\beta \bar{v}} (1 - a \rho_0) \exp \left[-\frac{a \rho_0}{1 - a \rho_0} \right], \quad (2.3)$$

and

$$\beta \Delta v(x) + \ln[\rho(x)/\rho_0] = \ln \left[1 - \gamma \int_{x-a}^x dy \Delta\rho(y) \right] - \gamma \int_x^{x+a} dz \left[\Delta\rho(z) + \gamma \rho_0 \int_{z-a}^z dy \Delta\rho(y) \right] \left[1 - \gamma \int_{z-a}^z dy \Delta\rho(y) \right]^{-1} \quad (2.4)$$

where $\gamma = (1 - a\rho_0)^{-1}$ and $\Delta v(x) = v(x) - \bar{v}$.

A few special cases are easy to discuss.

(i) $ak = 2\pi n$. If the hard-core diameter a is a multiple of the period $2\pi/k$ of the potential $v(x)$, then the integral

$$\int_{x-a}^x dy \Delta\rho(y) = a\rho_0 a_0 \quad (2.5)$$

is independent of x . Here, the spatial average of $\Delta\rho(x)$ has been denoted by $\rho_0 a_0$. Equation (2.4) now reads

$$\beta \Delta v(x) + \ln[\rho(x)/\rho_0] = \ln(1 - \gamma a \rho_0 a_0) - \frac{\gamma^2 a \rho_0 a_0}{1 - \gamma a \rho_0 a_0}, \quad (2.6)$$

which shows that $\rho(x)$ is proportional to $\exp[-\beta v(x)]$. The constants on the right-hand side of Eq. (2.6) together with Eq. (2.3) could be used to relate the fugacity to the average density $\bar{\rho} = \rho_0(1 + a_0)$.

(ii) *Slowly varying potential*. Let us assume that the potential $v(x)$ varies slowly over the distance a , implying $ak \ll 1$. Then the integral in Eq. (2.5) can be approximated by $a \Delta\rho(x)$. This leads to the local relationship

$$\rho(x) \approx \rho_0 e^{-\beta \Delta v(x)} [1 - \gamma a \Delta\rho(x)] \times \exp \left[-\frac{\gamma^2 a \Delta\rho(x)}{1 - \gamma a \Delta\rho(x)} \right]. \quad (2.7)$$

From Eq. (2.3) it can be shown that this is consistent with the thermodynamic equilibrium condition $\beta[v(x) + \mu(\rho(x))] = \text{const}$, where μ is the chemical potential as a function of density for the uniform system.

(iii) *Hypernetted chain approximation*. Let us define an effective potential $v_{\text{eff}}(x)$ through

$$\rho(x) = \text{const} \times \exp[-\beta v_{\text{eff}}(x)]. \quad (2.8)$$

The hypernetted chain (HNC) approximation can be regarded as an expansion of the difference $v_{\text{eff}}(x) - v(x)$ up to linear order in $\Delta\rho(x)$.¹² The general result is

$$-\beta[v_{\text{eff}}(x) - v(x)] = \int dy c_0(x-y, \rho_0) \Delta\rho(y), \quad (2.9)$$

where $c_0(x, \rho_0)$ denotes the direct correlation function of the uniform system. In fact, keeping only terms linear in $\Delta\rho$ on the right-hand side of Eq. (2.4), we obtain

$$\begin{aligned} \beta \Delta v(x) - \ln[\rho(x)/\rho_0] &= \gamma \int_{x-a}^{x+a} dy \Delta\rho(y) + \gamma^2 \rho_0 \int_x^{x+a} dz \int_{z-a}^z dy \Delta\rho(y) \\ &= \gamma \int_{x-a}^{x+a} dy [1 + \gamma \rho_0 (a - |x-y|)] \Delta\rho(y). \end{aligned} \quad (2.10)$$

This agrees with Eq. (2.9) in view of the expression

$$c_0(x, \rho_0) = \begin{cases} -\gamma[1 + \gamma \rho_0 (a - |x|)], & |x| < a \\ 0, & |x| > a \end{cases} \quad (2.11)$$

for the direct correlation function of a one-dimensional uniform hard-core fluid.³

In the linear-response (high-temperature) regime we have $\rho(x) \approx \rho_0 [1 - \beta v_{\text{eff}}(x)]$. Then Eq. (2.9) leads to the well-known relation

$$v_{\text{eff},n} = S_0(nk, \rho_0) v_n \quad (2.12)$$

between the Fourier components $v_{\text{eff},n}$ and v_n referring to the effective and the external potential, respectively. In Eq. (2.12), $S_0(k, \rho_0)$ denotes the static structure factor of the uniform fluid. For our special system we have¹³

$$S_0(k, \rho_0) = \left[1 + \frac{2\gamma\rho_0}{k} \sin(ka) + \frac{4\gamma^2\rho_0^2}{k^2} \sin^2 \left[\frac{ka}{2} \right] \right]^{-1}. \quad (2.13)$$

III. DENSITY-FUNCTIONAL THEORY

Before proceeding to our explicit calculations, we make a few remarks on the DFA and its application to our problem. The general method is based on an exact theorem⁵ which states that for a given pair interaction there exists a functional of the density, $\mathcal{F}[\rho]$, such that the equilibrium density in the presence of any external potential $v(\mathbf{r})$ is determined by minimizing the functional

$$\Omega_v[\rho] = \int d^3r \rho(\mathbf{r}) v(\mathbf{r}) + \mathcal{F}[\rho] - \mu \int d^3r \rho(\mathbf{r}). \quad (3.1)$$

At the minimum, $\Omega_v[\rho]$ is equal to the grand free energy of the system.

Various approximate forms for $\mathcal{F}[\rho]$ have been proposed.^{1,6} Here we consider the simple expression

$$\begin{aligned} \mathcal{F}[\rho] &= F_0(\bar{\rho}) + \beta^{-1} \int d^3r \rho(\mathbf{r}) \ln[\rho(\mathbf{r})/\bar{\rho}] \\ &\quad - (2\beta)^{-1} \int d^3r \int d^3r' c_0(\mathbf{r}-\mathbf{r}', \bar{\rho}) \\ &\quad \times [\rho(\mathbf{r}) - \bar{\rho}][\rho(\mathbf{r}') - \bar{\rho}], \end{aligned} \quad (3.2)$$

which consists in an expansion of $\mathcal{F}[\rho]$ up to the second order in density relative to its spatial average $\bar{\rho}$. In Eq. (3.2), $F_0(\bar{\rho})$ and $c_0(\mathbf{r}, \bar{\rho})$ are the Helmholtz free energy and the direct correlation function of a uniform fluid with density $\bar{\rho}$, respectively. These are input quantities assumed to be known.

Minimizing $\Omega_v[\rho]$ leads to the integral equation

$$\beta v(\mathbf{r}) + \ln[\rho(\mathbf{r})/\bar{\rho}] = \int d^3r' c_0(\mathbf{r}-\mathbf{r}', \bar{\rho}) [\rho(\mathbf{r}') - \bar{\rho}]. \quad (3.3)$$

$\bar{\rho}$ is a constant to be determined such that the solution $\rho(\mathbf{r})$ is consistent with a given $\bar{\rho}$. Equation (3.3) has the same form as the HNC equation (2.9) in connection with (2.8). Note, however, that the direct correlation function in Eq. (3.3) is taken at the average density $\bar{\rho}$ so that Eq. (3.3) is independent of any reference state.

In the next section we solve Eq. (3.3) for a one-dimensional hard-core fluid and calculate the corresponding free energy from Eq. (3.2).

IV. NUMERICAL RESULTS AND DISCUSSION

For our explicit calculations we assume an external potential $v(x)$ of the form

$$v(x) = v [1 + \cos(kx)]. \quad (4.1)$$

First we turn to the exact equation (2.4). Using the Fourier expansion

$$\Delta\rho(x) = \rho_0 \sum_{n (\geq 0)} a_n \cos(nkx), \quad (4.2)$$

we transform it into a set of equations for the coefficients a_n , which is solved by iteration. The truncation $n \leq N$ with $N = 7$ turned out to be sufficient for most of our results.

The density distribution $\rho(x)$ obtained in this way is most conveniently discussed in terms of the effective potential $v_{\text{eff}}(x)$ defined through Eq. (2.8). An interesting quantity is the effective potential amplitude $\Delta v_{\text{eff}} = [v_{\text{eff}}(0) - v_{\text{eff}}(\pi/k)]/2$. Its k dependence is shown by the full curve in Fig. 1 for the parameters $\beta v = 2$ and $\rho_0 a = 0.5$. Note that in solving Eq. (2.4) we have fixed ρ_0 for reasons of numerical convenience so that the average density $\bar{\rho} = \rho_0(1 + a_0)$ becomes k dependent, see Fig. 2.

According to Fig. 1, as k is varied, the system alternates between states where the density distribution is more localized ($\Delta v_{\text{eff}}/v > 1$) or more delocalized ($\Delta v_{\text{eff}}/v < 1$) as compared with the noninteracting case. The observed oscillatory behavior of the effective amplitude reflects the competition between the short-range correlation in the fluid and the periodicity of the external potential. This becomes most evident by noting that the effective amplitude closely follows the k dependence of the static structure factor $S_0(k, \rho_0)$, Eq. (2.13), which determines the effective amplitude in the linear-response regime according to $\Delta v_{\text{eff}}/v = S_0(k, \rho_0)$.

Now we turn to the corresponding predictions of the DFA. We have solved Eq. (3.4) in one dimension by using Fourier expansions, $c_0(x, \bar{\rho})$ being taken from Eq. (2.11). Results for the effective amplitude are shown in Fig. 1 by the dashed curve. The agreement with the accurate results (solid curve) is excellent, apart from a region in the neighborhood of $ak \sim 5$, where particle localization is most pronounced. There the DFA is in error by about 15%.

Explicit density profiles together with a plot of the potential $v_{\text{eff}}(x)$ are shown in Fig. 3 for the extremal cases $ak \simeq 4.8$ and 8. Note the relatively high density near the

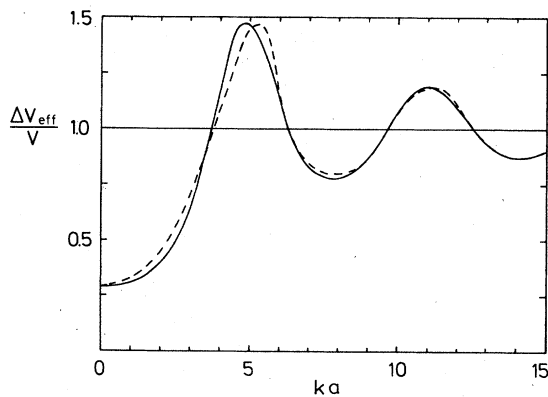


FIG. 1. Effective potential amplitude $\beta \Delta v_{\text{eff}}$ as a function of k (wave vector of the external potential) for the case $\beta v = 2$ and $\rho_0 a = 0.5$. (—), exact result and (---), DFA values.

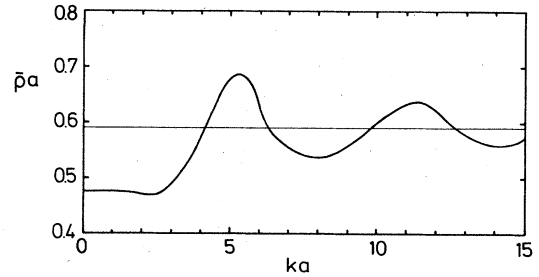


FIG. 2. Average density $\bar{\rho}a$ as a function of ka for the case $\beta v = 2$ and $\rho_0 a = 0.5$.

potential maximum in the incommensurate case of Fig. 3(b), which is well reproduced by the DFA.

Starting from Eq. (2.2) we have also calculated the Helmholtz free energy F , which is plotted in Fig. 4. The DFA free energy, obtained from Eq. (3.2) is higher by typically 0.5%, the largest deviation of about 2% occurring near $ak \sim 5$.

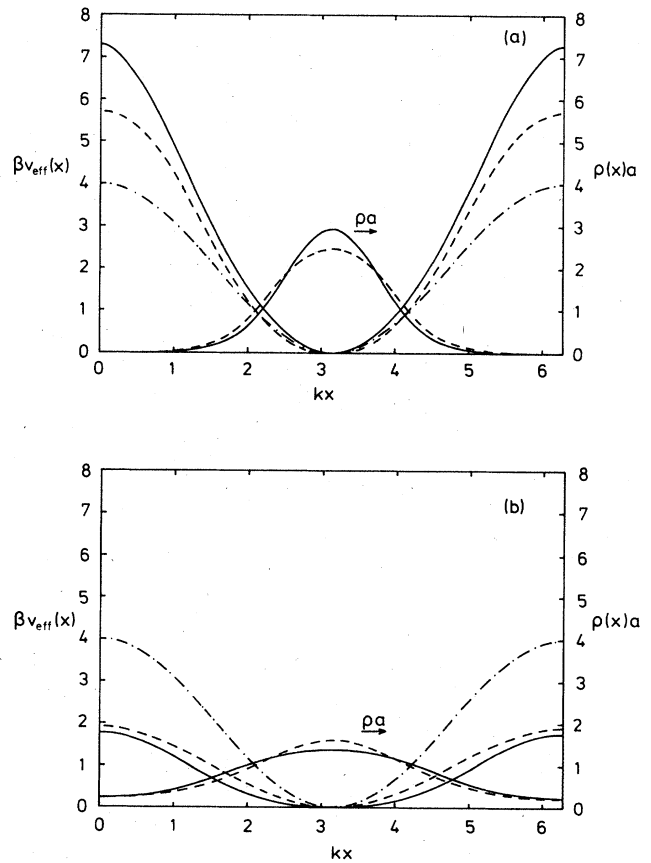


FIG. 3. Effective potential βv_{eff} and density profile ρa as a function of position. (—), exact results; (---), DFA values; and (- · - · -), external potential for the case $\beta v = 2$ and $\rho_0 a = 0.8$. (a) "Commensurate" case: $ka = 4.8$, $\bar{\rho}a = 0.763$; (b) "incommensurate" case: $ka = 8$, $\bar{\rho}a = 0.768$.

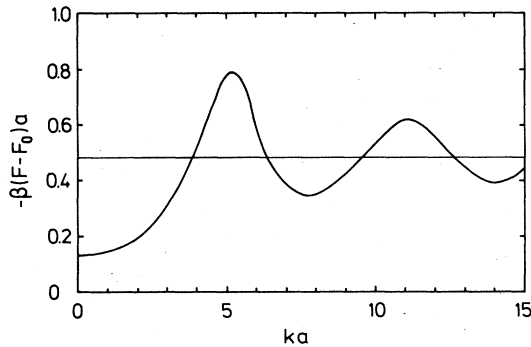


FIG. 4. Exact Helmholtz free energy βFa for the case $\beta v = 2$ and $\rho_0 a = 0.5$ as a function of ka .

Clearly, the DFA based on the functional Eq. (3.2) is expected to fail if the density distribution becomes more localized. In order to test this we have calculated the effective amplitude for some larger values of βv . Indeed, Fig. 5 shows that on increasing βv the DFA potential amplitudes become too low, and the corresponding density distributions will show insufficient structure.

Nevertheless, our results indicate that the functional Eq. (3.2) represents a sensible approximation in a rather

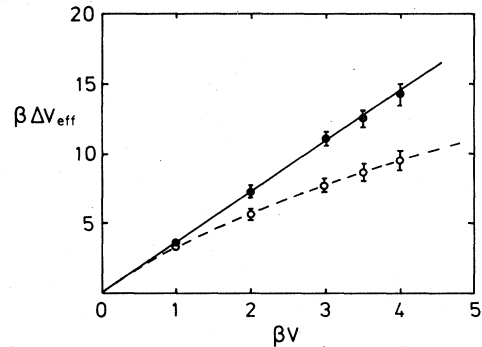


FIG. 5. Effective potential amplitude $\beta \Delta v_{\text{eff}}$ as a function of the external potential amplitude βv for $\rho_0 a = 0.8$. (●), exact results and (○), DFA values. The lines are guides to the eye.

wide range of parameters of physical interest. We expect that the range of applicability of the DFA found in the present study holds in a similar way also for higher-dimensional systems or more general interactions.

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