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Integral equation theory of a one dimensional hard-ellipse fluid between hard walls

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ABSTRACT

Density functional theory is used to study the structure of a one dimensional fluid model of hard-ellipse molecules with their axes freely rotating in a plane, confined between hard walls. A simple Hypernetted chain (HNC) approximation is used for the density functional of the fluid and the integral equation for the density is obtained from the grand potential. The only required input is the direct correlation function of the one dimensional hard-ellipse fluid. For this model, the pressure, sum rule and the density at the walls are obtained. The Percus Yevick (PY), for lower density, and HNC, for higher density, integral equations are also solved to obtain the direct correlation function of hard-ellipse model introduced here. We obtain the average density at the wall as well as the radial density profile. We compare these with Monte Carlo simulations of the same model and find reasonable agreement.

1. Introduction

Molecular liquid interacting through angle dependent pair potential may exhibit crystalline behavior [1–3]. This phase is called the mesophase, which is associated with the anisotropic character of the interaction between molecules. Liquid crystals are very useful for many applications due to their dual nature of easy response to surface force [4]. In the last decade the physics of confined liquid crystals [4,5] became an important subject from the technological point of view. The structure of atomic liquid is determined by the short range repulsive force acting between the atoms [6]. This is the main reason why the hard-sphere model is used widely in liquid theory. For more complex liquids such as liquid crystals, the structure is also primarily determined by the excluded volume effect [7]. The simplest, smooth nonspherical shapes are the ellipse and ellipsoids [8]. In the perturbative molecular fluid theory, the hard ellipsoids and hard ellipses are used as a reference system [9,10].

From a purely theoretical point of view, it is interesting to know how the molecular fluid and liquid-crystalline behavior depend on the confinement and dimensionality [11,12]. In this article, we are interested in studying the structural and thermodynamical properties of confined hard ellipses. Martinez-Haya and co-workers [13] obtained an analytical solution to a nonseparable interaction for a one-dimensional fluid model of anisotropic molecules and especially hard ellipses near hard wall. They studied a system of freely rotating hard ellipses with their center of mass restricted to move along a segment of a straight line confined between two parallel hard walls and computed the radial and angular profiles of the particles as well as the equation of state. Here, we use the molecular density functional theory to study these kinds of systems. As we will see in the following sections, by using density functional formalism, we are able to obtain the structural and thermodynamical properties of this system simply and accurately. In this theory, we introduce a grand potential of the system as a functional of the density and we use the HNC approximation.

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In Section 2, a one dimensional free energy functional is introduced and then minimized in order to get the integral equation for the density of ellipses.

In Section 3, an expression for a partial pressure of the ellipses in a given sector and from that the total pressure and density of the hard ellipses at the wall are obtained.

In Section 4 the PY and HNC integral equations for the hard ellipses are studied.

In Section 5 the results are shown and discussed.

2. One-dimensional density functional formalism

We consider a system of hard ellipses confined between two parallel hard walls and separated by a distance h. The center of the ellipses can move only in one dimension, the x direction, and x is zero midway between the walls. We choose x-axis perpendicular to the walls. In the HNC approximation the grand potential is given by [14]:

$$\beta\Omega[\rho] = \int \mathrm{d}x\mathrm{d}\omega\rho(x,\omega)\left[\ln\left(\frac{\omega_T\rho(x,\omega)}{\rho_B}\right)-1\right]+\beta\int \mathrm{d}x\mathrm{d}\omega\rho(x,\omega)V(x,\omega) - \frac{1}{2}\int \mathrm{d}x_1\mathrm{d}x_2\mathrm{d}\omega_1\mathrm{d}\omega_2\left(\rho(x_1,\omega_1)-\frac{\rho_B}{\omega_T}\right)\left(\rho(x_2,\omega_2)-\frac{\rho_B}{\omega_T}\right)c(x_1,x_2,\omega_1,\omega_2;\rho_B), \tag{1}$$

where $\rho(x,\omega)$ is the number density of molecules at position x with the major axes in the direction represented by ω. In this equation ρ_B is the bulk number density, $c(x_1,x_2,\omega_1,\omega_2)$ is the DCF of two molecules at position x_1 and x_2 with the major axes in the directions of ω_1 and ω_2 and $V(x,\omega)$ is the external potential. Here, the DCF of a one dimensional homogeneous ellipse fluid is required. This function can be obtained by PY and HNC integral equation theories for low and high number density respectively, and will be discussed. In Eq. (1) ω_T is the total angle available to each molecule,

$$\omega_T = \int \mathrm{d}\omega = 2\pi, \tag{2}$$

except near the walls and we discuss this matter later.

Here, we use the extension of the restricted orientation model (ROM) [15] and assume that each molecule can be aligned in N directions, $\omega_\alpha \equiv \theta_\alpha$, where θ_α is the angle of the major axis of the ellipses with respect to x-axis and defined as:

$$\theta_\alpha = \frac{2\pi\alpha}{N} \quad \alpha = 0, 1, \ldots, N-1, \tag{3}$$

$$\omega_T = \sum_{\alpha=0}^{N-1}\Delta\omega = N\Delta\omega = 2\pi. \tag{4}$$

The density component within a particular sector α is defined,

$$\rho_\alpha(x) = \int \mathrm{d}\theta\delta(\theta-\theta_\alpha)\rho(x,\theta), \tag{5}$$

where

$$\int \mathrm{d}\theta\rho(x,\theta) = \sum_{\alpha=0}^{N-1}\rho_\alpha(x). \tag{6}$$

In the case of homogeneous fluid,

$$\int \mathrm{d}\theta\rho(x,\theta) = \rho_B, \tag{7}$$

$$\rho_\alpha(x) = \frac{\rho_B}{N}. \tag{8}$$

Using the above equations, the grand potential for a system of the hard ellipses between parallel hard walls can be written as

$$\beta\Omega[\rho] = \sum_{\alpha=0}^{N-1}\int_{-\frac{h_\alpha}{2}}^{\frac{h_\alpha}{2}}\mathrm{d}x'\rho_\alpha(x')\left[\ln\left(\frac{\omega_T\rho_\alpha(x')}{\rho_B}\right)-1\right]+\sum_{\alpha=0}^{N-1}\int_{-\frac{h_\alpha}{2}}^{\frac{h_\alpha}{2}}\mathrm{d}x'\rho_\alpha(x')V(x',\theta_\alpha) - \frac{1}{2}\sum_{\alpha\beta}\int_{\frac{-h_\alpha}{2}}^{\frac{h_\alpha}{2}}\int_{\frac{-h_\beta}{2}}^{\frac{h_\beta}{2}}\mathrm{d}x'\mathrm{d}x''\left(\rho_\alpha(x')-\frac{\rho_B}{\omega_T}\right)\left(\rho_\beta(x'')-\frac{\rho_B}{\omega_T}\right)c_{\alpha\beta}(x',x''), \tag{9}$$

where,

$$h_\alpha = h-b-(a-b)|\cos(\theta_\alpha)|, \tag{10}$$