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# New equations of state for hard disk fluid by asymptotic expansion method

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**Abstract**

Using the newly introduced asymptotic expansion method to obtain equations of state for hard sphere fluid, new simple equations of state for hard disks based on known virial coefficients are derived. Comparison of the obtained equations of state with computer simulation data shows that they are accurate in the whole fluid region.


*Keywords:* Equations of state; Hard disk fluid; Asymptotic expansion method

## 1. Introduction

Hard disk fluid plays an important role in description of some phenomena in surface science. For example in a very recent study an equation of state of hard disk fluid has been used along with a version of statistical associating fluid theory in order to describe the adsorption of fluids on solid surfaces [1]. For this reason its thermodynamic properties has been studied by various methods; e.g. scaled particle theory [2], and calculation of its virial coefficients [3,4]. By these methods one can obtain the most important quantity of interest; the equation of state, by which one can calculate all thermodynamic properties. Over the years many equations of state for hard disks have been proposed that were compared with together and with molecular dynamics data [5]. Importance of understanding the behavior of hard disks is such that new investigations in the form of computer simulations are continuously performed, for example [6]. Along with these investigations we would like to use the newly introduced asymptotic expansion method [7] to obtain new equations of state for hard disks. Thus in subsequent section, we briefly introduce the asymptotic expansion method. Then in the later section we will obtain new equations of state based on first several known virial coefficients of hard disks. In the last section we compare new equations of state with some of the best previous ones and with the computer simulation data.

## 2. The asymptotic expansion method

We have previously introduced the asymptotic expansion method to obtain accurate equations of state for hard spheres [7]. In this method we start from known virial coefficients and write

$$Z = 1 + B_2\eta + B_3\eta^2 + B_4\eta^3 + \cdots \tag{1}$$

where $Z$ (=$P/\rho kT$) is the compressibility factor, $\eta$ (=$(\pi/4)\rho\sigma^2$) the packing fraction, $\rho$ the number density, $P$ the pressure, $T$ the absolute temperature, $\sigma$ the diameter of hard disk, and $k$ is the Boltzmann constant. We may notice that if Eq. (1) should represent the properties of a real fluid, it must be convergent. Suppose the radius of convergence of the virial expansion is $b$; therefore $\eta$ must be less than $b$, because for $\eta \geq b$ the virial expansion becomes divergent, i.e., it cannot represent a real system. Since we are unable to obtain and calculate all virial coefficients, we can only hope to obtain an approximation. By now, all that we know besides knowing first several virial coefficients is that it must be divergent at $\eta \geq b$.

So one can deduce that $b$ is a *pole* for the compressibility factor $Z = Z(\eta)$. Taking this fact into account we may write the

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*asymptotic expansion* of Z, which is of the form:

$$Z = a_0 + \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} + \frac{a_3}{(\eta - b)^3} + \cdots \tag{2}$$

Adopting this form for the asymptotic expansion of Z, and then expanding into virial form and comparison with first known several virial coefficients, one can easily arrive at many equations of state for hard disk fluid. One may note that this method is similar to the mapping approach of Yelash and Kraska to obtain new equations of state for hard sphere fluid [8].

## 3. Some equations of state for hard disks based on virial coefficients

As we may know the first several virial coefficients of the hard disk fluid are [6]: $B_2 = 2$, $B_3 = 3.1280$, $B_4 = 4.2579$, $B_5 = 5.3369$, $B_6 = 6.3630$, $B_7 = 7.3521$, $B_8 = 8.3187$, $B_9 = 9.2723$, and $B_{10} = 10.2161$.

Since we are not aware of the exact value of $b$ at which the virial expansion, Eq. (1), becomes divergent, we are free to choose it conveniently. Since maximum close packing of hard disks occurs at $\eta = 0.9069$ [5], one may assume any value for $b$ greater than 0.9069, say, $b = 1$, besides this we cannot say anymore. In addition to this, the number of terms in asymptotic expansion, Eq. (2), is another degree of freedom we have. For example, if we restrict ourselves to use only the first four known virial coefficients, we should select those asymptotic expansion forms with only four unknowns. But in order to find more rigorous representations for equation of state, one should know and use more virial coefficients; hence more possibilities for the form of asymptotic expansions are there to be tried. As soon as selecting a definite value for $b$ and the number of terms in the asymptotic expansion representation of Z, say four terms like Eq. (10) in the following, one is able to obtain the desired coefficients, which are related to $b$, the pole. Different $b$'s produce different coefficients, but up to fourth order of course, they are all the same. They produce approximate (and different) values for the remainder terms. Among them one must be the best, but this method cannot achieve this important goal alone. At best we can resort to approximate theories like Scaled Particle Theory which asserts that $b = 1$, or approximately determine it by the known virial coefficients.

(A) Suppose that the asymptotic form of the compressibility factor Z to be:

$$Z = a_0 + \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} \tag{3}$$

Expanding Eq. (3) in powers of $\eta$ gives:

$$Z = \left(a_0 - \frac{a_1}{b} + \frac{a_2}{b^2}\right) + \left(-\frac{a_1}{b^2} + \frac{2a_2}{b^3}\right)\eta + \left(-\frac{a_1}{b^3} + \frac{3a_2}{b^4}\right)\eta^2 + O(\eta^3) \tag{4}$$

Equating these coefficients with known second and third virial coefficients gives:

$$\begin{cases} a_0 - \dfrac{a_1}{b} + \dfrac{a_2}{b^2} & = & 1 \\ -\dfrac{a_1}{b^2} + \dfrac{2a_2}{b^3} & = & B_2 \\ -\dfrac{a_1}{b^3} + \dfrac{3a_2}{b^4} & = & B_3 \end{cases} \tag{5}$$

Its solution is:

$$\begin{cases} a_0 = & 1 - 2B_2 b + B_3 b^2 \\ a_1 = & -3B_2 b^2 + 2B_3 b^3 \\ a_2 = & -B_2 b^3 + B_3 b^4 \end{cases} \tag{6}$$

Inserting these values in Eq. (3) and collecting we finally obtain:

$$Z = \frac{(1 - 2B_2 b + B_3 b^2)\eta^2 + (B_2 b^2 - 2b)\eta + b^2}{(\eta - b)^2} \tag{7}$$

Now we may put $b = 1$(together with $B_2 = 2$ and $B_3 = 3$) in Eq. (7) which gives:

$$Z_8 = \frac{1}{(1 - \eta)^2} \tag{8}$$

This is the well-known equation of state of Scaled Particle Theory obtained by Helfand et al. [2].

(B) We may put the accurate values of the second and third virial coefficients, i.e., $B_2 = 2$ and $B_3 = 3.128$ into Eq. (7) to obtain

$$Z_9 = \frac{0.128\,\eta^2 + 1}{(\eta - 1)^2} \tag{9}$$

This was previously derived by Henderson [9].

(C) We may proceed one step further and suppose that the asymptotic form of Z is:

$$Z = a_0 + \frac{a_1}{\eta - b} + \frac{a_2}{(\eta - b)^2} + \frac{a_3}{(\eta - b)^3} \tag{10}$$

Assuming $b = 1$ we have this time four unknowns, hence need to employ up to fourth virial coefficients. Proceeding as before, one obtains:

$$Z_{11} = \frac{-1.0000 - 0.1280\eta^2 + 1.0000\eta + 0.1261\eta^3}{(\eta - 1)^3} \tag{11}$$

As an alternative we suppose $b = 1.1$ to obtain:

$$Z_{12} = \frac{-1.3310 - 0.2034\eta^2 + 0.9680\eta + 0.0874\eta^3}{(\eta - 1.1000)^3} \tag{12}$$

Until now, the choice of the radius of convergence ($b$) was arbitrary. But we can determine $b$ from the virial coefficients; hence there is indeed no need to assume it freely. It is obvious that if we take $b$ as another unknown, we are able to find it.

(D) First step is to choose Eq. (3) which may be expanded in powers of $\eta$ up to fourth order. Equating the coefficients with known first four virial coefficients gives:

$$\begin{cases} \dfrac{2a_2}{b_3} - \dfrac{a_1}{b^2} & = & 2 \\ \dfrac{3a_2}{b^4} - \dfrac{a_1}{b^3} & = & 3.128 \\ \dfrac{4a_2}{b^5} - \dfrac{a_1}{b^4} & = & 4.2579 \end{cases} \quad . \tag{13}$$

This system of equations has two set of solutions.

The first set is:

$b = 0.4701, \qquad a_0 = -0.1891, \qquad a_1 = -0.6760,$

$a_2 = -0.0550$

and the second one:

$b = 0.9992, \qquad a_0 = 0.1261, \qquad a_1 = 0.2503,$

$a_2 = 1.1225$

Since we would like to have $b$ as large as possible we must choose the second set. Inserting these values in Eq. (3) and collecting them, one obtains the desired equation:

$$Z_{14} = \frac{0.1261\eta^2 - 0.0017\eta + 0.9983}{(\eta - 0.9992)^2} \tag{14}$$

(E) As second step we will use Eq. (10) which may be expanded in powers of $\eta$ up to fifth order. Equating the coefficients with known virial coefficients gives:

$$\begin{cases} \dfrac{a_0 - a_1}{b} + \dfrac{a_2}{b^2} - \dfrac{a_3}{b^3} & = & 1 \\ -\dfrac{a_1}{b^2} + \dfrac{2a_2}{b^3} - \dfrac{3a_3}{b^4} & = & 2 \\ -\dfrac{a_1}{b^3} + \dfrac{3a_2}{b^4} - \dfrac{6a_3}{b^5} & = & 3.128 \\ -\dfrac{a_1}{b^4} + \dfrac{4a_2}{b^5} - \dfrac{10a_3}{b^6} & = & 4.2579 \\ -\dfrac{a_1}{b^5} + \dfrac{5a_2}{b^6} - \dfrac{15a_3}{b^7} & = & 5.3369 \end{cases} \tag{15}$$

This system of equations has three set of solutions.

The first two sets are:

$b = 0.3730, \qquad a_0 = -0.1534, \qquad a_1 = -0.6182,$

$a_2 = -0.0836, \qquad a_3 = -0.0050$

$b = 0.8842, \qquad a_0 = 0.0879, \qquad a_1 = 0.1092,$

$a_2 = 0.9497, \qquad a_3 = 0.1239$

These are rejected in favor of the third set:

$b = 1.1363, \qquad a_0 = 0.0516, \qquad a_1 = -0.0751,$

$a_2 = 0.5686, \qquad a_3 = -0.6483$

Inserting these values in Eq. (10) and collecting them, one obtains another equation for hard disks:

$$Z_{16} = \frac{0.0516\eta^3 - 0.2511\eta^2 + 0.9392\eta - 1.4670}{(\eta - 1.1363)^3} \tag{16}$$

## 4. Comparison of the equations of state with computer simulation data

Now that we have found some simple equations of state for hard disk fluid we must check their accuracy by comparing with some other equations of state and with computer simulation data. Santos et al. [5] have suggested a simple equation of state, namely:

$$Z_{17} = \frac{1}{1 - 2\eta + ((2\eta_0 - 1)\eta^2)/\eta_0^2} \tag{17}$$

where $\eta_0 = \sqrt{3}\pi/6$ is the value for the maximum close packing. By comparison with the most known equations of state for hard disks [9–14], the authors showed Eq. (17) has the highest accuracy among simple equations. Thus, it is enough to compare the equations obtained here with Eq. (17) and with computer simulation data. For Monte Carlo data we have used the accurate data of Erpenbeck and Luban [13] as reproduced in [5]. The whole fluid range of hard disks is not covered by these data. For completeness we have also used the newer data of Kolafa and Rottner [6] for higher densities up to the freezing point ($\eta_F = 0.70$ [15]). The results have been given in Fig. 1. As may be seen some of the obtained equations of state here, for example Eqs. (12) and (16) are much more accurate than Eq. (17). We may further demonstrate this result by comparing the predicted virial coefficients with the precise ones reported in [6]. The results of such comparison have been shown in Table 1. We can once again observe that the simple equations derived by asymptotic expansion method are superior than Eq. (17).

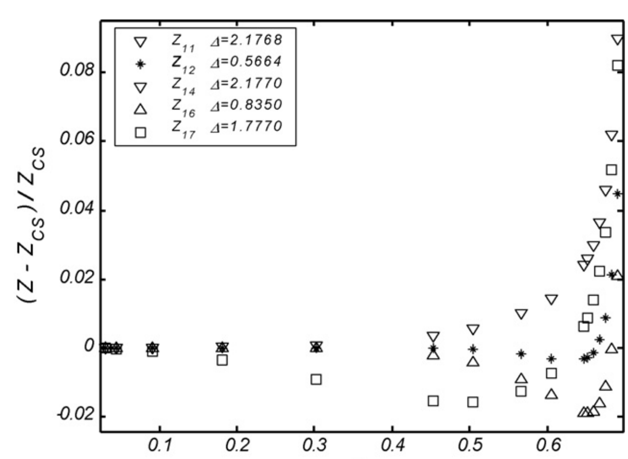


Fig. 1. Relative deviation curves of the obtained hard disk equations of state with computer simulation data. Also $\Delta (= (100/N)\sum_{j=1}^{N}|Z_{MD}(\eta_j) - Z(\eta_j)|/Z_{MD}(\eta_j))$ is the average fractional deviation from the computer simulation data.

Table 1
Comparison of the virial coefficients of the obtained hard disk equations of state with computer simulation (CS) data

| Virial coefficients | $Z_{CS}$ [a] | $Z_{11}$ | $Z_{12}$ | $Z_{14}$ | $Z_{16}$ |
|---|---|---|---|---|---|
| $B_2$ | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 |
| $B_3$ | 3.1280 | 3.1280 | 3.1280 | 3.1280 | 3.1280 |
| $B_4$ | 4.2579 | 4.2579 | 4.2579 | 4.2579 | 4.2579 |
| $B_5$ | 5.3369 | 5.3897 | 5.3597 | 5.3897 | 5.3369 |
| $B_6$ | 6.3630 | 6.5234 | 6.4107 | 6.5234 | 6.3292 |
| $B_7$ | 7.3521 | 7.6590 | 7.3943 | 7.6590 | 7.2120 |
| $B_8$ | 8.3187 | 8.7965 | 8.2987 | 8.7965 | 7.9728 |
| $B_9$ | 9.2723 | 9.9359 | 9.1164 | 9.9360 | 8.6064 |
| $B_{10}$ | 10.2161 | 11.0772 | 9.8430 | 11.0773 | 9.1133 |

[a] Taken from ref. [6].

## 5. Conclusion

Using the newly introduced asymptotic expansion method to obtain equations of state for hard sphere fluid, new simple equations of state for hard disks based on known virial coefficients are derived. Comparison of the obtained equations of state with computer simulation data and the predicted virial coefficients with exact values shows that the equations despite their simplicity are very accurate in the whole fluid region.

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