

An accurate and simple equation of state for hard disks

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An equation of state for a fluid of hard disks is proposed: $Z = [1 - 2\eta + (2\eta_0 - 1)(\eta/\eta_0)^2]^{-1}$. The exact fit of the second virial coefficient and the existence of a single pole singularity at the close-packing fraction η_0 are the only requirements imposed on its construction. A comparison of the prediction of virial coefficients and of the values of the compressibility factor Z with those stemming out of other known equations of state is made. The overall performance of this very simple equation of state is quite satisfactory. © 1995 American Institute of Physics.

I. INTRODUCTION

Hard disks and hard spheres represent model systems useful for the derivation of rigorous results in statistical mechanics as well as in a perturbation treatment of fluids.¹ In particular, the coefficients B_n appearing in the virial equation of state

$$Z \equiv \frac{p}{\rho kT} = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + \dots \quad (1)$$

(where p is the pressure, ρ is the number density, k is the Boltzmann constant, and T is the temperature) are easier to compute in these systems than for any other intermolecular potential. Nevertheless, the number of cluster integrals involved increases so rapidly with order that only the first few of such coefficients have been calculated so far. In fact, it took over twenty-five years to go from the seventh² to the eighth.³ Also, refinements of B_5 , B_6 and B_7 , which are not known analytically, were performed during this period.⁴ As is well known, taking just the truncated power series is not a very convenient method of approximating the compressibility factor Z , especially for moderate and high densities.¹ Therefore, it is not surprising that many efforts have been devoted to the search of better analytical equations of state for these systems. Loosely speaking, one may identify within these efforts two main lines of approach. On the one hand, there is a set of equations of state, which we shall refer to as “complex,” whose aim is geared towards accuracy, either in reproducing a number of known virial coefficients^{2,3,5–12} or fitting simulation results.¹³ On the other hand, in the second approach, equations of state are proposed or derived in which accuracy may be sacrificed in favor of analytical simplicity or the inclusion of only a reduced number of fitting parameters. We will call these “simple.” The prototypes in this set are the ones arising in the scaled-particle theory¹⁴ and in the free volume approximation¹⁵ as well as closely related derivations.^{7,16–21} And of course the success of the Carnahan–Starling²² equation of state for hard spheres, which may also be obtained by combining the compressibility and virial equations of state arising in the Percus–Yevick theory,²³ is undeniable.

The fact that no analytical solution of the Percus–Yevick equation for hard disks is known has prevented the derivation of a two-dimensional analog of the Carnahan–Starling equation, although some attempts in the same spirit have been reported.^{7,18–20} Given the vast amount of work pertaining to the subject already available in the literature (of which our references are by no means an exhaustive list) the proposal of yet another equation of state for hard disks, as done below, seems hardly justifiable. However, the present belief that the pressure of the fluid diverges at the crystalline close-packing density^{8,9} (in spite of some controversy)²⁴ together with the recent analysis of Sanchez,¹² which suggests that the virial series contains information about this divergence, prompted us to take such a step. In the spirit of a generalized (two-point) Padé approximant,²⁵ we now propose a very simple equation of state for hard disks that yields the exact second virial coefficient and has a pole at the density of crystalline close-packing, namely

$$Z = \left[1 - 2\eta + \frac{2\eta_0 - 1}{\eta_0^2} \eta^2 \right]^{-1}, \quad (2)$$

where $\eta = (\pi/4) \rho \sigma^2$ is the packing fraction and $\eta_0 = (\sqrt{3}/6) \pi$ is the value corresponding to crystalline close-packing. The merits and limitations of this proposal are best judged from a comparison with simulation data and other equations of state. To this end, we select a few “simple” and “complex” equations from the literature and compute the compressibility factor and the prediction of virial coefficients up to B_8 and beyond.

II. COMPRESSIBILITY FACTOR AND VIRIAL COEFFICIENTS

With the purpose of making the paper self-contained, we start this section by quoting, in a unified notation, the equations of state that we will compare to ours. In increasing order of complexity, we consider the following:

1. Scaled particle theory (SPT)¹⁴

$$Z = \frac{1}{(1 - \eta)^2}; \quad (3)$$

2. Henderson (H)^{18–20}

$$Z = \frac{1 + \alpha_H \eta^2}{(1 - \eta)^2}, \quad (4)$$

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TABLE I. Virial coefficients b_n as obtained from Eq. (3) (SPT), Eq. (2) (this work), Eq. (4) (H), Eq. (5) (A), Eq. (6) (B-L), Eq. (7) (W), Eq. (8) [Levin (6)], and Eq. (9) [Padé (3,4)]. Entries with an asterisk indicate that the equation of state yields the corresponding known virial coefficient by construction.

n	Known ^a	SPT	This work	H	A	B-L	W	Levin (6)	Padé (3,4)
2	2	*	*	*	*	*	*	*	*
3	3.12801775	3	3.011	*	*	*	*	*	*
4	4.25785446	4	4.042	4.256	3.912	*	*	*	*
5	5.336897	5	5.105	5.384	4.569	*	*	*	*
6	6.3626	6	6.211	6.512	5.203	*	*	*	*
7	7.351	7	7.371	7.640	5.861	7.392	7.190	7.346	*
8	8.338	8	8.596	8.768	6.563	8.462	7.928	8.300	*
9	—	9	9.899	9.896	7.324	9.598	8.742	9.239	9.348
10	—	10	11.293	11.024	8.152	10.818	9.639	10.175	10.426

^aReference 3.

where $\alpha_H = b_3 - 3 = \frac{7}{3} - (4\sqrt{3}/\pi) \approx 0.1280$ and we have introduced the reduced virial coefficients $b_n = B_n / (B_2/2)^{n-1}$;

3. Andrews (A)¹⁷

$$Z = \frac{3\eta}{(1-\eta/\eta_0)(1-\alpha_A\eta)} - \frac{1}{\eta} \ln(1-\eta) - \frac{3\eta_0}{\alpha_A\eta} \ln(1-\alpha_A\eta) + \frac{3\eta_0^2}{(1-\alpha_A\eta_0)\eta} \ln \frac{1-\eta/\eta_0}{1-\alpha_A\eta}, \quad (5)$$

with $\alpha_A = \frac{1}{2}(b_3 - \frac{1}{3}) - \eta_0^{-1} = \frac{5}{2} - (4\sqrt{3}/\pi) \approx 0.2947$;

4. Baram and Luban (B-L)⁸

$$Z = \frac{C}{1-\eta/\eta_0} + \frac{D\eta_0}{\eta} \ln(1-\eta/\eta_0) + \sum_{n=1}^4 \left(b_n \eta_0^{n-1} - C + \frac{D}{n} \right) \times (\eta/\eta_0)^{n-1}, \quad (6)$$

where $C = \eta_0^4(6b_6\eta_0 - 5b_5)$ and $D = 30\eta_0^4(b_6\eta_0 - b_5)$;

5. Woodcock (W)⁶

$$Z = \frac{1+3\eta/\eta_0}{1-\eta/\eta_0} + \sum_{n=2}^6 (b_n - 4)(\eta/\eta_0)^{n-1}; \quad (7)$$

6. Levin (6) approximant¹⁰

$$Z = \frac{\sum_{n=0}^4 p_n \eta^n}{\sum_{n=0}^5 q_n \eta^n}, \quad (8)$$

with $q_n = (-1)^n \binom{6}{n} (1-n/6)^5 b_6 / b_{6-n}$ and $p_n = \sum_{m=0}^n b_{n+1-m} q_m$;

7. Padé (3,4) approximant¹²

$$Z = \frac{\sum_{n=0}^3 r_n \eta^n}{\sum_{n=0}^4 s_n \eta^n}, \quad (9)$$

where the coefficients r_n and s_n are obtained as to reproduce the virial coefficients through b_8 .

The first three of these equations belong to the simple class, while the others are complex. In Table I we list the virial coefficients b_n up to $n=10$ as obtained from the different equations of state and compare them with the currently known values.³ We have arranged the columns preserving the order of complexity and so the third column contains the values from our proposal. On comparing these values, it is clear that Eq. (2) not only provides reasonable estimates of the virial coefficients, but also performs better than some of the more complex equations with a minimum of input. For instance, it is striking that the seventh virial coefficient predicted by Eq. (2) is more accurate than the one coming from Eqs. (6) or (7), which explicitly include up to the sixth coefficient in their construction.

While the results we have just mentioned are already suggestive, a more indicative source of performance is the analysis of the compressibility factor. This is done in Table II. Here, we have included the simulation data of Erpenbeck and Luban,¹⁰ which are considered the most accurate pres-

TABLE II. Compressibility factor Z as obtained from simulation and from the same equations of state as in Table I.

η_0/η	Simulation ^a	SPT	This work	H	A	B-L	W	Levin (6)	Padé (3,4)
1.4	8.306	8.061	8.359	8.494	7.625	8.465	8.290	8.343	8.409
1.5	6.6074	6.396	6.558	6.696	6.126	6.663	6.574	6.609	6.635
1.6	5.4963	5.329	5.427	5.548	5.155	5.522	5.473	5.495	5.507
1.8	4.1715	4.062	4.107	4.194	3.984	4.179	4.161	4.171	4.174
2.0	3.4243	3.348	3.372	3.436	3.311	3.427	3.420	3.424	3.425
3.0	2.0771	2.054	2.058	2.078	2.057	2.077	2.077	2.077	2.077
5.0	1.4983	1.492	1.493	1.499	1.495	1.498	1.498	1.498	1.498
10.0	1.21068	1.2094	1.2095	1.2107	1.2104	1.2107	1.2107	1.2107	1.2107
20.0	1.09743	1.0973	1.0973	1.0975	1.0975	1.0975	1.0975	1.0975	1.0975
30.0	1.06337	1.06332	1.06333	1.06344	1.06343	1.06344	1.06344	1.06344	1.06344

^aReference 10.

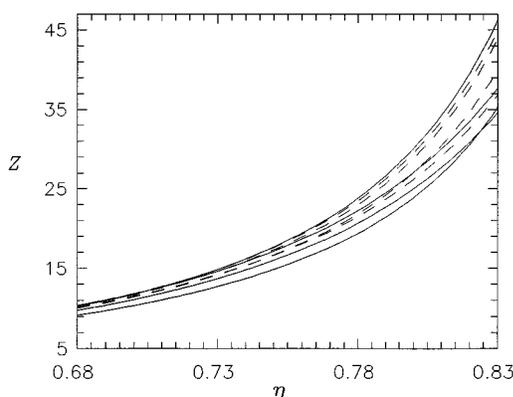


FIG. 1. Compressibility factor Z vs the packing fraction η in an interval comprising the metastable fluid region. From top to bottom at the right end, the curves correspond to Eq. (2) (this work), Eq. (6) (B-L), Eq. (9) [Padé (3,4)], Eq. (7) (W), Eq. (4) (H), Eq. (8) [Levin (6)], Eq. (5) (A), and Eq. (3) (SPT). The solid lines refer to “simple” equations, while the dashed lines refer to “complex” equations.

ently available. One can see that Eq. (2) does a good job over the whole density range and is clearly superior to the other simple, and even to some of the complex equations, for the higher densities. It is worthwhile to stress that the relative error incurred through the use of this equation is always less than 1.5 % within the interval of densities considered. Given the fact that beyond $\eta_0/\eta = 1.6$ this relative error decreases dramatically, it is interesting to compare the various equations at even higher densities. Therefore in Fig. 1 we have plotted the compressibility factor as a function of packing fraction as given from all the equations of state appearing in Tables I and II. The density interval goes from a little bit below the freezing packing fraction ($\eta_F \approx 0.70$)²⁶ up to that of random close-packing ($\eta_{RCP} \approx 0.82$)²⁷ and so it contains the metastable fluid region. Here one can easily see that Eq. (2) is wholly consistent with the Padé (3,4) approximant, which is considered by Sanchez¹² to be very accurate, and that only Eq. (6) also shares this consistency for all densities. This is in our opinion rather impressive in view of the simplicity of the equation that we are proposing.

III. DISCUSSION

The results presented above deserve some additional comments. It should be clear at this stage that in spite of its simplicity, Eq. (2) works extremely well for all densities. The key idea behind its construction is to slightly modify the SPT equation of state, Eq. (3), retaining the merits of this equation for the low-density behavior (ours also yields the exact second virial coefficient) and incorporating the high-density divergence at close-packing. As a consequence, the double pole at $\eta = 1$ in Eq. (3) was replaced by two simple poles at $\eta = \eta_0$ and $\eta = \eta_0/(2\eta_0 - 1)$ in Eq. (2). It should be pointed out that the equation proposed by Henderson, Eq. (4), was also meant as a minor modification of the SPT equation. However, the emphasis was on fitting the third virial coefficient, which is related to low- and moderate-density fluid behavior, but left the pole at $\eta = 1$. In some sense, then, the main difference between these two proposals is that ours

includes the global behavior of the virial series as determined by the divergence at close packing,¹² while Henderson’s focuses on a specific coefficient. One should be cautious, however, in thinking that taking into account the singularity at close packing is enough to devise an accurate equation of state. In fact, the equation proposed by Andrews, Eq. (5), which contains this feature as well as fitting the third virial coefficient by construction, does not perform better than the SPT equation.

We have mentioned in the Introduction that the hard-disk model is a useful tool for the analysis of many problems in statistical mechanics. Therefore, the availability of an accurate and simple equation of state, such as Eq. (2), may be very valuable if one wants to deal with problems near or inside the metastable fluid region, in a perturbation treatment of two-dimensional fluids, etc. For instance, in the application of the generalized effective liquid approximation to hard-disk freezing²⁶ one needs the excess free energy, and this quantity may be readily derived from Eq. (2) as

$$\begin{aligned} \frac{A_{\text{ex}}}{NkT} &= \int_0^\eta d\eta' \frac{Z(\eta') - 1}{\eta'} \\ &= \frac{(2\eta_0 - 1) \ln \left(1 - \frac{2\eta_0 - 1}{\eta_0} \eta \right) - \ln(1 - \eta/\eta_0)}{2(1 - \eta_0)}. \end{aligned} \quad (10)$$

Also, very recently the adsorption kinetics of disks to a smooth two-dimensional surface has been analyzed in terms of the activity coefficient $\gamma(\eta) = \exp(-1 + A_{\text{ex}}/NkT)$ evaluated through the eight term virial series.²⁸ A similar analysis could be carried out using the activity coefficient obtained from Eqs. (2) and (10).

Finally, it is interesting to mention that if the same approach were used for a hard-rod system, the resulting equation of state would be the exact one. However, if one wants to take a similar route in the case of hard spheres the outcome is not so satisfactory.

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