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Equations of state for the classical hard-sphere fluid

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A newly developed thermodynamic approach based on excluded volume is applied to the classical hard-sphere fluid to derive a new precise equation of state for the entire density range.

A new theory of the equation of state based on excluded volume has been formulated recently[1–4] and used for deriving equations of state well applicable to the gaseous region. Using dimensionless variables, the main quantity of the theory was the exclusion factor

$$f \equiv v^{\text{ex}}/v_0 \tag{1}$$

as the ratio of the excluded volume v^{ex} to the molecular volume v_0, both of the volumes being understood as average quantities in case of a multicomponent system. Three approximations of the theory were considered. The zero approximation implied the exclusion factor to be constant and led to the Planck equation of state for a monatomic gas. The first approximation assumed the exclusion factor to be a linearly decreasing function of the (total) packing fraction φ and reproduced the van der Waals equation of state. The second approximation approached the real behaviour of $f(\varphi)$ (which is a concavely decreasing function) by using the simplest linear-fraction function

$$f = \frac{f_0 - k_1\varphi}{1 + k_2\varphi}, \tag{2}$$

where f_0 is the limiting value of the exclusion factor for a rarified gaseous state ($f_0 = 8$ for a single species) and k_1 and k_2 are positive constants. The values of the constants were chosen as to satisfy two requirements, the accuracy and simplicity of an equation of state. For example, the van der Waals equation was the simplest among the solutions of a master equation of the theory in the first approximation. Similarly, the requirement of simplicity led to a combination of the Planck and van der Waals equations in the second approximation. Since ascending the hierarchy of approximations widens the range of applicability of an equation of state, the derivation of an equation of state for the entire density range requires considering higher approximations of the theory of excluded volume, and this is the aim of this work.

When considering gases, we attained an accuracy by calculating the coefficients k_1 and k_2 from the second and third virial coefficients. Turning now to the entire density range, we have to address to standard data for this region, for example, to the classical molecular dynamics data published by Alder and Wainwright[5] for hard spheres. The additional reason for it is that these data were used for verifying the Carnahan–Starling equation for the hard-sphere fluid[6]

$$Z \equiv \frac{pv}{k_\text{B}T} = \frac{\tilde{p}}{\varphi} = \frac{1 + \varphi + \varphi^2 - \varphi^3}{(1 - \varphi)^3}, \tag{3}$$

where Z is the compressibility factor, p is the pressure, v is the volume per molecule in the system, k_B is the Boltzmann constant, T is the temperature, and $\tilde{p}$ is the reduced pressure. Up to the present time, the Carnahan–Starling equation has a reputation of the most accurate equation of state for hard spheres. Therefore, it is interesting to compare the equations of state resulting from the excluded volume theory with the Carnahan–Starling equation.

Table 1 Values of k and the coefficient of determination in the hierarchy of approximations.

Approximation number	k	Coefficient of determination
3	1.283681	0.997342
4	1.070709	0.999457
5	0.918766	0.999847
6	0.805259	0.999945
7	0.717260	0.999946

For the particular case of a fluid of hard spheres of equal sizes, the master equation of the excluded volume theory is

$$\tilde{p} = \int_0^{\varphi} \frac{\mathrm{d}\varphi}{1 - f\varphi}, \tag{4}$$

The equation of state in the second approximation was obtained by putting (2) into equation (4). The algorithm of further approximations will be chosen as follows: at each step, we shall add a higher-order term ($k_3\varphi^2$, $k_4\varphi^3$, $k_5\varphi^4$, *etc.*) to the numerator of equation (2), the denominator being maintained unchanged in the form (but with a variable value of k_2). After putting the resultant expression for f into (4), the values of the constants will be chosen so as to reduce the integral to the simplest form. In the third approximation, for example, we have

$$f^{(3)} = \frac{8 - k_1\varphi + k_3\varphi^2}{1 + k_2\varphi}, \tag{5}$$

$$\tilde{p}^{(3)} = \int_0^{\varphi} \frac{(1 + k_2\varphi)\mathrm{d}\varphi}{1 - (8 - k_2)\varphi + k_1\varphi^2 - k_3\varphi^3}, \tag{6}$$

Setting $k_1 = 3k^2$, $k_2 = 8 - 3k$, and $k_3 = k^3$ changes the denominator of the integrand in (6) to $(1 - k\varphi)^3$, where k is a new (still unknown) constant. The integration yields

$$\tilde{p}^{(3)} = \frac{\varphi - 2(k-2)\varphi^2}{(1 - k\varphi)^2}, \quad Z^{(3)} = \frac{\tilde{p}^{(3)}}{\varphi} = \frac{1 - 2(k-2)\varphi}{(1 - k\varphi)^2}, \tag{7}$$

which is the equation of state in the third approximation. With $k = 1$, equation (7) takes the form

$$Z^{(3)} = \frac{1 + 2\varphi}{(1 - \varphi)^2}, \tag{8}$$

which is a truncated form of the pressure variant of the Percus–Yevick equation of state[7]

$$Z = \frac{1 + 2\varphi + 3\varphi^2}{(1 - \varphi)^2}, \tag{9}$$

The general formula for an equation of state in the nth approximation ($n \geq 3$) is

$$Z^{(n)} = \frac{1}{(1 - k\varphi)^{n-1}}\left\{1 - \frac{2k(n-1) - 8}{(n-1)(\text{n}-2)k^2\varphi}[(1 - k\varphi)^{n-1} - 1 + (\text{n}-1)k\varphi]\right\}. \tag{10}$$

Equation (10) changes to (7) at $n = 3$. At $n = 4$, equation (10) changes to the equation of state in the fourth approximation

$$Z^{(4)} = \frac{1 - (3k - 4)\varphi + k(k - 4/3)\varphi^2}{(1 - k\varphi)^3}. \tag{11}$$

With $k = 1$, equation (11) takes the form

$$Z^{(4)} = \frac{1 + \varphi - \varphi^2/3}{(1 - \varphi)^3}, \tag{12}$$

which is comparable with both the Carnahan–Starling equation (3) and the compressibility variant of the Percus–Yevick equation of state[7–9]

$$Z = \frac{1 + \varphi - \varphi^2}{(1 - \varphi)^3}. \tag{13}$$

Turning to the fifth approximation ($n = 5$), equation (10) yields the following equation of state:

$$Z = \frac{1 - (2/3)(k-1)(6\varphi - 4k\varphi^2 + k_2\varphi^3)}{(1-k\varphi)^4}. \tag{14}$$

If $k = 1$, (14) changes to the empirical Guggenheim equation of state[10]

$$Z = \frac{1}{(1-\varphi)^4}, \tag{15}$$

which seems to be the shortest form of an equation of state.

It is easy to verify that equation (10) yields the proper value 4 for the second virial coefficient irrespective of a k-value. This secures the applicability of equation (10) to the gaseous state and gives a possibility for applying equation (10) to the dense range by varying the constant k. An appropriate value of k in each approximation can be found by fitting a resultant equation of state the standard data.[5] Table 1 shows how the k-value and the coefficient of determination change in the approximation hierarchy. It is also seen that the coefficient of determination is practically the same for the sixth and seventh approximations exhibiting a very high degree of precision. That was the reason for aborting further computation.

Table 2 exhibits the numerical values of the compressibility factor computed for the same density values as used by Alder and Wainwright[5] (v_∞ is the value of v at the closest hexagonal packing, so that $v/v_\infty = \pi\sqrt{2}/6\varphi$) whose data are presented in column 8. For comparison, column 9 of Table 2 displays the results published by Carnahan and Starling.[6] As is seen in Table 2, the Carnahan–Starling equation has no advantage in accuracy with respect to equation (10).

Among the approximations presented, of special interest is the sixth approximation looking numerically as

$$Z^{(6)} = \frac{1 - 0.026(\varphi - 0.805\varphi^2 + 0.324\varphi^3 - 0.052\varphi^4)}{(1-k\varphi)^5}, \tag{16}$$

where the k-value shown in Table 1 has been used. Because the coefficient 0.026 is small, the approximation $Z \approx Z_0^{(6)}$ is possible, where

$$Z_0^{(6)} = \frac{1}{(1-k\varphi)^5}, \tag{17}$$

The k-value in (17) can be precised by repeating the fitting procedure. This yields $k = 0.803025293$ with the coefficient of determination 0.999952, which is higher than any other value in Table 1. It is sufficient to set $k = 0.803$ to suggest a new equation of state for hard spheres:

$$Z = (1 - 0.803\varphi)^{-5}. \tag{18}$$

Table 2 Numerical presentation of equation of state (10).

v/v_∞	φ	$Z^{(3)}$	$Z^{(4)}$	$Z^{(5)}$	$Z^{(6)}$	$Z^{(7)}$	Z^{AW}	Z^{CS}	$Z_0^{(6)}$
1.5	0.494	12.72	12.60	12.53	12.49	12.46	12.5	12.43	12.48
1.6	0.463	10.09	10.16	10.19	10.21	10.22	10.17	10.16	10.21
1.7	0.436	8.36	8.49	8.56	8.60	8.63	8.59	8.56	8.60
2	0.370	5.56	5.70	5.78	5.83	5.86	5.89	5.83	5.84
3	0.247	2.90	2.96	2.99	3.01	3.03	3.05	3.03	3.02
10	0.074	1.35	1.35	1.36	1.36	1.36	1.36	1.36	1.36

Equation (18) has been tabulated in the last column of Table 2. Comparing with the Carnahan–Starling equation, equation (18) is behind in two lines, but wins in three lines of Table 2. Therefore, one may speak about the advantage of equation (18) in accuracy. As for simplicity, equation (18) is only comparable with Guggenheim equation (15).

The above analysis can be repeated with any other set of standard data. The main conclusion is that the excluded volume theory yields a precise equation of state for a classical hard-sphere fluid in the entire density range.

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