The equation of state of hard hyperspheres in four and five dimensions

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The equation of state of hard hyperspheres in four and five dimensions is calculated from the value of the pair correlation function at contact, as determined by Monte Carlo simulations. These results are compared to equations of state obtained by molecular dynamics and theoretical approaches. In all cases the agreement is excellent.
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The equation of state of simple fluids has been an active object of research for many years. Investigators have approached its study by using a variety of methods. On the theoretical side, various representations of fluid behavior have been proposed. One such important theoretical method is the virial expansion of the equation of state:[1]

$$Z_V = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + B_5\rho^4 + \cdots B_{V+1}\rho^V. \tag{1}$$

Here, the compressibility factor Z_V is defined as

$$Z_V = P\beta/\rho, \tag{2}$$

where β is $1/k_BT$ (k_B is Boltzmann's constant and T is the absolute temperature), P is the pressure, and ρ is the reduced number density. In the case of hard hyperspheres Z_V is independent of the temperature since the virial coefficients (B_V, $V=2,3,\ldots$) are independent of temperature. A number of the B's (B_2, B_3, and B_4) are known exactly[2,3] for D dimensional hyperspheres because the necessary multidimensional integrals can be evaluated analytically. Other values (B_5, B_6, B_7, B_8, B_9, and B_{10}) are known[3–8] from extensive numerical calculations.

The equation of state, Z as a function of ρ, in D dimensions (see the Appendix) is related to the contact value of the pair correlation function $G(\sigma)$ by

$$Z = 1 + \rho B_2 G(\sigma), \tag{3}$$

where σ is the diameter of the D dimensional hypersphere and B_2 is the second virial coefficient. It has the value[2] of

$$B_2 = \frac{\pi^{D/2}\sigma^D}{2\Gamma(1+D/2)}, \tag{4}$$

where Γ is the Gamma function.

In a previous publication[9] we have reported on our SWC (SmallWeb computing) Java framework Monte Carlo (MC) computer simulations. In that work we obtained $G(\sigma)$ for hard hyperspheres where D ranged from one to five. The contact value of the pair correlation function, $G(R)$, was determined by fitting a least-squares line[10] to the first five data points for which the separation R is larger than 1.00. The equation of this line was then evaluated at the point $R=1.00$ to find the contact value. The error bar on the contact value was determined by the error bars on the fitted coefficients of the straight line. These MC numerical results for $G(\sigma)$ were compared to the theoretical equation of Song, Mason, and Stratt[11] which predicted $G(\sigma)$ at any arbitrary dimension and density,

$$G(\sigma) = \frac{1-\alpha\eta}{(1-\eta)^D}, \tag{5}$$

where η is the packing fraction

$$\eta = \frac{B_2\rho}{2^{D-1}} \tag{6}$$

and

$$\alpha = D - 2^{D-1}\frac{B_3}{B_2^2}. \tag{7}$$

Here B_3 is the third virial coefficient.

They derived this equation, using mean field theory, based on the Carnahan–Starling equation of state[12] and assumed the probability that a second particle will be found within a small region about a reference particle is the product of independent probabilities for each dimension. Excellent agreement between their theory and the MC data was found in all dimensions studied.

Since the equation of state results are well known in one, two, and three dimensions, here we only report our new findings for four and five dimensions. The $G(\sigma)$ results are used to determine the equation of state via Eq. (3). These MC values are compared to the molecular dynamics (MD) data of Luban and Michels[13] and Lue.[14] Moreover, the most accurate new values of B_8, B_9, and B_{10}[5,6] are used to obtain theoretical predictions of the virial equation of state in four and five dimensions, as was recently done by Bishop, Masters, and Vlasov[7] using only lower order B_V values (up to B_8 in four dimensions and B_7 in five dimensions).

In all of this work, the hard hypersphere diameter is set to one and therefore, all quantities are reported in reduced units. The Z_V expansion, Eq. (1), includes the (V+1)th virial coefficient. Using all the known values for B_V, Z_9 has been

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computed in both four and five dimensions. Using the notation that $[n,m]$ indicates an approximant that has a polynomial of degree n for its numerator and a polynomial of degree m for its denominator, both the [4,5] and [5,4] Padé approximates in four and five dimensions were determined from the virial expansions. The Padé approximates are one way of more accurately representing the virial power series.

In four dimensions we find that

$$Z_{[4,5]} = \frac{1 + 2.0618\rho + 1.5498\rho^2 + 0.1215\rho^3 - 0.3273\rho^4}{1 - 0.4056\rho - 0.5320\rho^2 + 0.4036\rho^3 - 0.0813\rho^4 - 0.0007\rho^5}, \quad (8)$$

$$Z_{[5,4]} = \frac{1 + 2.0539\rho + 1.5338\rho^2 + 0.1099\rho^3 - 0.3276\rho^4 + 0.0029\rho^5}{1 - 0.4135\rho - 0.5285\rho^2 + 0.4078\rho^3 - 0.0846\rho^4}, \quad (9)$$

whereas in five dimensions that

$$Z_{[4,5]} = \frac{1 + 5.6285\rho + 11.4725\rho^2 + 10.5480\rho^3 + 3.6629\rho^4}{1 + 2.9966\rho + 0.7176\rho^2 - 1.3205\rho^3 + 0.3080\rho^4 - 0.0039\rho^5}, \quad (10)$$

$$Z_{[5,4]} = \frac{1 + 5.6390\rho + 11.5374\rho^2 + 10.6878\rho^3 + 3.7971\rho^4 + 0.0486\rho^5}{1 + 3.0071\rho + 0.7549\rho^2 - 1.3089\rho^3 + 0.2903\rho^4}. \quad (11)$$

Figure 1 presents Z vs ρ for four dimensional hyperspheres. All the MC simulation data is in excellent agreement with the MD data and the theoretical [4,5] and [5,4] Padé approximates. Similar excellent agreement among the MC, MD, and Padé approximates is revealed in Fig. 2 for five dimensional hyperspheres. Preliminary comparisons using virial coefficients only up to order B_6 had discrepancies in the equation of state at higher densities. The current fine agreement is the result of the availability of the higher order virial coefficients.

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APPENDIX: EQUATION OF STATE OF HARD HYPERSPHERES IN ARBITRARY DIMENSION

The relationship between the equation of state and the pair correlation function at contact, $G(\sigma)$, follows from the D dimensional form of the pressure equation:[1]

$$Z = 1 - (\beta\rho/2D) \int G(R)R[\partial U(R)/\partial R]d\mathbf{R}. \quad (A1)$$

The first term in this Eq. (1) is the ideal gas contribution. The second term is caused by particle interactions. The pair potential of D dimensional hyperspheres with diameter σ separated by the D dimensional distance R is given by

$$U(R) = \begin{cases} \infty, & R < \sigma \\ 0, & R \geqslant \sigma \end{cases}. \quad (A2)$$

In Eq. (A1), $\partial U(R)/\partial R$ is the derivative of the pair potential and $d\mathbf{R}$ is the D dimensional differential volume element. Now consider the general Meyer f function,[1]

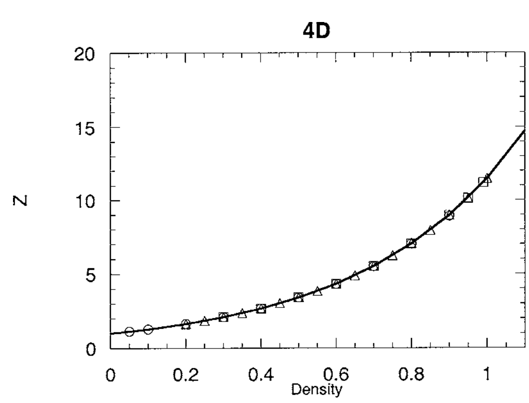

FIG. 1. Equation of state in four dimensions: MC (○), MD (Ref. 13) (△), MD (Ref. 14) (□), $Z_{[4,5]}$ Padé (—), $Z_{[5,4]}$ Padé (···).

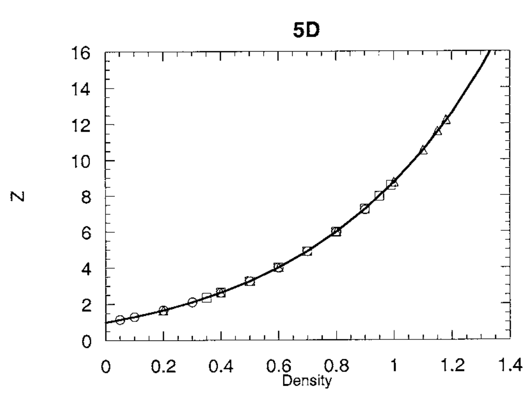

FIG. 2. Equation of state in five dimensions: MC (○), MD (Ref. 13) (△), MD (Ref. 14) (□), $Z_{[4,5]}$ Padé (—), $Z_{[5,4]}$ Padé (···).

$$f(R) = \exp[-\beta U(R)]. \tag{A3}$$

From the chain rule, one finds that

$$\partial f(R)/\partial R = [\partial f(R)/\partial U(R)][\partial U(R)/\partial R] = -\beta \exp(-\beta U(R))[\partial U(R)/\partial R] \tag{A4}$$

but in the special case of hard hyperspheres:

$$f(R) = \begin{cases} 0, & R < \sigma \\ 1, & R \geqslant \sigma \end{cases}. \tag{A5}$$

This is the Heavyside step function and its derivative is the delta function.[15] One may then replace $\partial f(R)/\partial R$ by $\delta(R-\sigma)$ and rearrange terms to obtain

$$\partial U(R)/\partial R = -\exp[\beta U(R)]\delta(R-\sigma)/\beta. \tag{A6}$$

The differential volume element $d\mathbf{R}$ is given by the surface area, S_D times $d\mathbf{R}$. The surface area of a D dimensional hypersphere is[16]

$$S_D = \frac{\pi^{D/2} D R^{D-1}}{\Gamma(1+D/2)}. \tag{A7}$$

Substituting for $\partial U(R)/\partial R$ in Eq. (A1) one obtains

$$Z = 1 + \frac{(\rho/2)\pi^{D/2} G(\sigma)\sigma^D}{\Gamma(1+D/2)}. \tag{A8}$$

But the second virial coefficient B_2 is known[2] to be

$$B_2 = \frac{\pi^{D/2}\sigma^D}{2\Gamma(1+D/2)}. \tag{A9}$$

Hence, the equation of state in all dimensions is given by

$$Z = 1 + \rho B_2 G(\sigma). \tag{A10}$$

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