

Equation of State for a Dense Rigid Sphere Gas from Basic Equations of Statistical Mechanics

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Durch geeignete Auswertung der Zustandssumme für ein Hartkugelgas (N Kugeln vom Durchmesser σ im Volumen V bei der Temperatur T) wird als Zustandsgleichung

$$p/R T = \varepsilon/(V-b) - [(\varepsilon-1)/b] \ln[V/(V-b)]$$

gewonnen. Darin bedeuten $\varepsilon = 8\pi/3 \sqrt{2} - 1$ und $b = N\sigma^3/\sqrt{2}$, das Volumen bei dichtester Kugelpackung. Im Vergleich mit der Virialentwicklung und anderer Näherungen liefert diese Zustandsgleichung die dichteste Kugelpackung $V=b$ als Grenzdichte. Für mittlere Dichten wird der Druck etwas zu klein, jedoch sind die Abweichungen von der Virialentwicklung nicht größer als bei den bekannten anderen Näherungen. Für geringe Dichte treten praktisch keine Abweichungen zur Virialentwicklung auf. In einer Virialentwicklung führt die Zustandsgleichung zu durchweg positiven Virialkoeffizienten, für den zweiten Virialkoeffizienten wird der exakte Wert erhalten.

1. Introduction

The rigid sphere gas has found great interest as a starting point in the theory of liquids and as a model, with which we can proof several approximations for the equation of state. At low densities the virial expansion gives the exact behavior of the gas. It is wrong for a dense gas, because we don't get a limit density. In other approximations¹, valid also for moderate density as the YVON-BORN-GREEN equation (YBG), the PERCUS-YEVICK equation (PY), the KIRKWOOD equation (K) or the hypernetted chain equation (HNC), we have to solve integral equations. They don't lead to an equation of state in a simple mathematical form and to a critical density except for special cases. Here an equation of state is developed from the basic equations of statistical mechanics, which gives a good fit for low and high densities, which leads to the closest packing density as the limit density, and which has a useful and relatively simple mathematical form.

2. Basic Equations

We get the equation of state from the partition function for a system of N particles and temperature T in a box of volume V

$$Z_N = \int \frac{d\mathbf{r}_1 \dots d\mathbf{r}_N}{N! h^{3N}} \exp\{-\beta H_N\} = \frac{1}{N! \lambda^{3N}} Q_N, \quad \beta = 1/k T, \quad (1)$$

$$Q_N = \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp\{-\beta U_N\}, \quad U_N = \sum_{i < j}^N u(i, j)$$

by differentiation

$$\frac{p}{k T} = \frac{\partial \ln Z_N}{\partial V} = \frac{\partial \ln Q_N}{\partial V}. \quad (2)$$

For evaluating Q_N we write

$$Q_N = V q_{N-1} Q_{N-1} = V^N \prod_0^{N-1} q_n = V^N \exp\left(\int_0^N dn \ln q_n\right) \quad (Q_0 = 1). \quad (3)$$

Then we get as definition for q_n

$$q_n = \frac{Q_{n+1}}{V Q_n} = \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_n \exp\{-\beta U_n\} (1/V) \int d\mathbf{s} \exp\{-\beta \tilde{U}_n\}}{\int d\mathbf{r}_1 \dots d\mathbf{r}_n \exp\{-\beta U_n\}} \equiv \left\langle \frac{1}{V} \int d\mathbf{s} \exp\{-\beta \tilde{U}_n\} \right\rangle_n, \quad \tilde{U}_n = \sum_{i=1}^n u(i, s), \quad (4)$$

where $\langle \rangle_n$ is a mean value over all configurations of n particles. With $f_{is} = \exp(-u_{is}/k T) - 1$ and (2), (3) and (4) the equation of state is to be calculated from

$$\frac{p V}{N k T} = 1 + \frac{V}{N} \frac{\partial}{\partial V} \int_0^N dn \ln q_n \quad (5)$$

$$q_n = \left\langle \frac{1}{V} \int d\mathbf{s} \prod_{i=1}^n (1 + f_{is}) \right\rangle_n.$$

¹ A resume we find in S. A. RICE and P. GRAY, The Statistical Mechanics of Simple Liquids, Intersci. Publ., New York 1965.



3. Application to the Hard Sphere Gas

Now we consider a gas of rigid spheres of diameter σ so that $f_{is} = -\theta(\sigma - r_{is})$. Therefore, for a given configuration r_1, \dots, r_n (s. Fig. 1) the integrand of $V_f^{(n)} = \int d\mathbf{s} \prod_{i=1}^n (1 + f_{is})$ vanishes in spheres of radius σ with the centres r_1, \dots, r_n and is one otherwise. This means that $V_f^{(n)}$ is the integral over all points, on which we can put the particle "s" if n particles are at the points r_1, \dots, r_n . For q_n (5) we can write

$$q_n = \langle V_f^{(n)} / V \rangle_n. \quad (6)$$

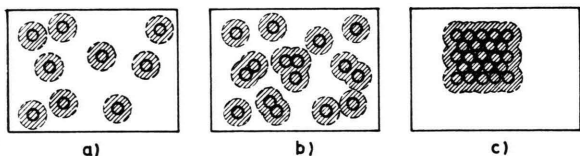


Fig. 1. $V_f^{(n)}$ is the volume, which is not hatched. a), b) c) show different configurations of the particles $1, \dots, n$. The hatched spheres have the diameter 2σ .

The lowest value for $V_f^{(n)}$ we get, if the spheres $r_{is} \leq \sigma$ of volume $\tilde{v} = 4\pi\sigma^3/3$ do not overlap (see Fig. 1 a). It is

$$\min V_f^{(n)} = V - n\tilde{v} \text{ or zero.} \quad (7)$$

The upper value of $V_f^{(n)}$ we get, if all n spheres are in closest packing in a volume

$$n v_d \quad (v_d = 3\sqrt{2}\tilde{v}/8\pi),$$

so that (s. Fig. 1 c)

$$\max V_f^{(n)} = V - n v_d. \quad (8)$$

From (7) and (8) we see that for q_n holds

$$1 - \frac{n}{N} \tilde{v} \varrho \leq q_n(\varrho) \leq 1 - \frac{n}{N} v_d \varrho. \quad (9)$$

So we can discuss, what we expect for q_n (6) by different densities $\varrho = N/V$ (s. Fig. 2).

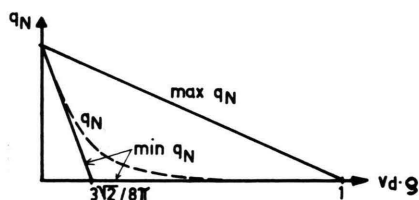


Fig. 2. Discussion of the density dependence of q_N .

At low densities configurations with overlapping spheres $r_{is} \leq \sigma$ are very rare so that $q_n \approx \min q_n$. At high density also configurations of type 1 b) are more probable than configurations of type 1 c). This means that $q_n = 0$ holds for most configurations, for some q_n is small but different from zero. The mean value lies near zero. Therefore we expect the dotted line of Fig. 2 for q_n . It shall be calculated in the following.

4. Hard Sphere Gas at low Density

At sufficiently low density q_n (6) is equal to $\min q_n$. This means an approximation, where two-particle correlations between pairs (i, s) are taken into account exactly and higher correlations are approximated by the demand that all configurations with higher correlations are forbidden. It leads to

$$\begin{aligned} \ln Q_N^0(\tilde{v}) &= N \ln V + \int d\mathbf{n} \ln \left(1 - \frac{n}{N} \tilde{v} \varrho \right) \\ &= N \ln V - N \frac{1 - \tilde{v} \varrho}{\tilde{v} \varrho} \ln(1 - \tilde{v} \varrho) - N, \end{aligned} \quad (10)$$

$$p/kT = - (1/\tilde{v}) \ln(1 - \tilde{v} \varrho). \quad (11)$$

This equation of state (11) was first derived by PLANCK². It has the right second virial coefficient $B = N\tilde{v}/2$, but it is better than the virial expansion $p/kT = \varrho + \tilde{v}\varrho^2/2$, because it leads to a critical value for the density. Due to the approximation it is not yet the right critical density, but it is too low.

5. The Dense Gas in the One-Dimensional Case

In a three-dimensional system calculations in the dense case are very hard. Therefore we first consider a one-dimensional system, where we can solve the problem exactly³.

Let's look at a system of n rods of length l_d on a straightline of length L (s. Fig. 3). We introduce coordinates x_i as the distance of the edges between the particles $i-1$ and i . Then the x_i run from 0 to l_n with the restriction

$$\sum_{i=1}^n x_i = l_n, \quad l_n = L - n l_d. \quad (12)$$

For a given configuration x_1, \dots, x_n we want to put a rod "s" on the line. The integration over all

² M. PLANCK, Physikalische Abhandlungen und Vorträge, Bd. II, Vieweg & Sohn, Braunschweig 1958, p. 221.

³ A resume we find in A. MÜNSTER, Statistische Thermodynamik, Springer-Verlag, Berlin 1956, p. 237.

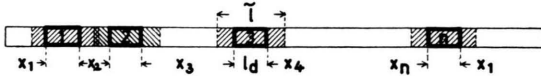


Fig. 3. n rods on a straightline characterised by coordinates x_i . If x_i is smaller than l_d , no additional rod can be put between the rods $i-1$ and i .

points, where we can put (the centre of) the particle s gives the length $L_f^{(n)}$. From Fig. 3 we see that one particle covers a length $\tilde{l} = 2l_d$, so that only $x_i - (\tilde{l} - l_d) = x_i - l_d$ contributes to $L_f^{(n)}$. But if $x_i - l_d < 0$ then we cannot put a rod between the particles $i-1$ and i . So we have

$$L_f^{(n)} = \sum_{i=1}^n [x_i - (\tilde{l} - l_d)] \theta[x_i - (\tilde{l} - l_d)], \quad (13)$$

where $\theta(x)$ is the step function.

Now we calculate the mean value of $L_f^{(n)}$ over all configurations with the restriction (12)

$$\begin{aligned} \langle L_f^{(n)} / L \rangle_n &= \frac{1}{L} \left\langle \sum_{i=1}^n [x_i - (\tilde{l} - l_d)] \theta[x_i - (\tilde{l} - l_d)] \right\rangle_n \\ &= \frac{n}{L} \langle [x_1 - (\tilde{l} - l_d)] \theta[x_1 - (\tilde{l} - l_d)] \rangle_n \\ &= \frac{n}{L} \frac{\int_0^{l_n} dx_1 [x_1 - (\tilde{l} - l_d)] \theta[x_1 - (\tilde{l} - l_d)] \int_0^{l_n - x_1} dx_2 \dots \int_0^{l_n - x_1 - \dots - x_{n-1}} dx_n}{\int_0^{l_n} dx_1 \int_0^{l_n - x_1} dx_2 \dots \int_0^{l_n - x_1 - \dots - x_{n-1}} dx_n} \\ &= \frac{n}{n+1} \frac{[l_n - (\tilde{l} - l_d)]^{n+1}}{L l_n^n} \\ &= \frac{n}{n+1} \left(1 - \frac{n l_d}{L}\right) \left(1 - \frac{(\tilde{l} - l_d)}{L - n l_d}\right)^n. \end{aligned}$$

For large n we get

$$\langle L_f^{(n)} / L \rangle_n = \left(1 - \frac{n l_d}{L}\right) \exp \left[- \frac{n(\tilde{l} - l_d)}{L - n l_d} \right]. \quad (14)$$

This result holds for all densities. For the closest packing $L = n l_d$ $\langle L_f^{(n)} \rangle_n$ goes extremely to zero and for low density we get $\langle L_f^{(n)} \rangle_n = L - n \tilde{l}$.

6. Dense Hard Sphere Gas in the Three-Dimensional Case

In the three-dimensional case an exact evaluation of q_n is not possible. Therefore we extend the functional form (14) of the density dependence of q_n from the one-dimensional case to the three-dimensional case. This extension may be done, because $V_f^{(n)}$ and $L_f^{(n)}$ have the same signification. Further on their values in the occurring configurations are

very similar. For high density $V_f^{(n)}$ and $L_f^{(n)}$ are for most configurations zero and only for some configurations different from zero. Naturally this does not mean that also the equations of state are very similar. The one-dimensional system contains restrictions for the movement of the particles, which do not occur in the three-dimensional case. Therefore the equation of state may not be extended.

So we get as the extension of (14)

$$q_n = \left(1 - \frac{n v_d}{V}\right) \exp \left[- \frac{n(\tilde{v} - v_d)}{V - n v_d} \right]. \quad (15)$$

In the three-dimensional case the spheres $r_{is} \leq \sigma$ also overlap in three dimensions not only in one dimension. This causes that $\tilde{v} = (8\pi/3\sqrt{2}) v_d \approx 6 v_d$ holds instead of $\tilde{l} = 2 l_d$. q_n from (15) exponentially goes to zero for the closest packing and becomes $q_n = 1 - n \tilde{v}/V$ for the low density case.

With $\tilde{v} - v_d = \varepsilon v_d$, $\varepsilon = 8\pi/3\sqrt{2} - 1$, we get from (3) and (15)

$$Q_N = V^N \prod_{i=0}^{N-1} \left(1 - \frac{n v_d}{V}\right) \exp \left[- \varepsilon v_d \sum_{i=0}^{N-1} \left(\frac{n}{V - n v_d}\right) \right]. \quad (16)$$

with

$$\begin{aligned} - \sum_{i=0}^{N-1} \frac{n}{V - n v_d} &= \frac{d}{dv_d} \sum_{i=0}^{N-1} \ln(V - n v_d) \\ &= \frac{d}{dv_d} \ln V^N \prod_{i=0}^{N-1} \left(1 - \frac{n v_d}{V}\right) \end{aligned}$$

we can Q_N reduce to Q_N^0 (10)

$$Q_N = Q_N^0(v_d) \exp \left[\varepsilon v_d \frac{d}{dv_d} \ln Q_N^0(v_d) \right],$$

$$\ln Q_N = \left(1 + \varepsilon v_d \frac{d}{dv_d}\right) \ln Q_N^0(v_d).$$

For the derivation of Q_N we get with (11)

$$\frac{\partial \ln Q_N}{\partial V} = - \left(1 + \varepsilon v_d \frac{d}{dv_d}\right) \frac{1}{v_d} \ln(1 - v_d \varrho),$$

and for the equation of state we find finally

$$\begin{aligned} \frac{p}{k T \varrho} &= \frac{\varepsilon}{1 - v_d \varrho} - \frac{1 - \varepsilon}{v_d \varrho} \ln(1 - v_d \varrho), \\ \varepsilon &= \frac{8\pi}{3\sqrt{2}} - 1 \end{aligned} \quad (17)$$

ore with $N v_b \equiv b$

$$\frac{p}{R T} = \frac{\varepsilon}{V - b} - \frac{\varepsilon - 1}{b} \ln \frac{V}{V - b}.$$

This equation of state gives the closest packing as critical density and the right second virial coefficient.

In the one-dimensional case we have to choose $\varepsilon = 1$. So we get a VAN DER WAALS equation as derived by TONKS⁴.

7. Discussion of the Results

In Fig. 4 we compare some equations of state for the hard sphere system. We have drawn Equ. (17), the virial expansion up to the sixth coefficient and solutions of the integral equations for the pair distribution from KIRKWOOD (K), PERCUS-YEVICK (PY) and from the hypernetted-chain approximation (HNC). From this integral equations we get two solutions. In the solution (p) the equation of state is calculated directly from the pair distribution, in the solution (c) the compressibility is calculated first and then the equation of state by thermodynamic relations.

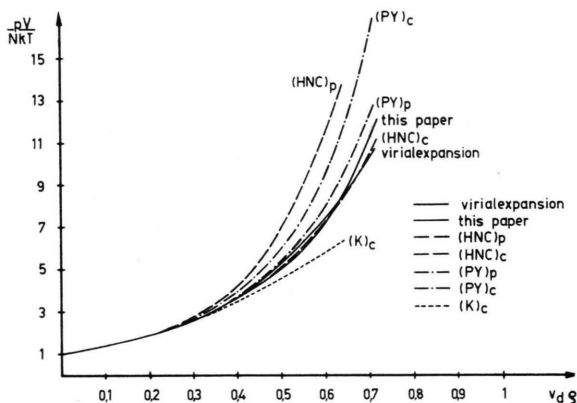


Fig. 4. Different solutions for the equation of state for a system of hard spheres⁵.

⁵ The values for the other approximations are taken from RICE¹.

⁴ L. TONKS, Phys. Rev. **50**, 955 [1936].

The critical density lies at $v_d \varrho = 1$. For low density up to $v_d \varrho \approx 0.3$ there is no difference between (17) and the virial expansion. For moderate density $v_d \varrho \approx 0.3 \dots 0.65$ (17) leads to a somewhat too low pressure, but the deviation is small, especially not larger than the deviations of the other approximations. And for those approximations we don't know, whether we have to choose solution (p) or (c). For high density $v_d \varrho \geq 0.65$ (17) is better than the virial expansion. For $v_d \varrho = 1$ the pressure goes to infinity.

We also can consider the virial expansion of (17). We get

$$\frac{p}{k T \varrho} = \sum_{n=1}^{\infty} \frac{1 + (n-1) \varepsilon}{n} (v_d \varrho)^{n-1} \quad (18)$$

$$= \sum_{n=1}^{\infty} \frac{1 + (n-1) \varepsilon}{n} \left(\frac{2}{\varepsilon + 1} \right)^{n-1} \left(\frac{\tilde{v} \varrho}{2} \right)^{n-1}.$$

The virial coefficients are all positive and compared in Table 1.

Solution	B	$C/(B_0)^2$	$D/(B_0)^3$	$E/(B_0)^4$
exact	$N \tilde{v}/2 = B_0$	5/8	0,2869	0,1103
(17)	$N \tilde{v}/2$	0,412	0,1513	0,0534

Table 1. Comparison of virial coefficients for a hard sphere gas.

The integral equations are results of cluster summations and the clusters up to third order are taken into account exactly, so that they lead to the exact third virial coefficient. But we see from Fig. 4 that there is no essential influence of the third virial coefficient on the equation of state at low density, and at higher density we must not consider single virial coefficients but the equation of state on the whole.

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