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A SIMPLE EQUATION IN THE THEORY OF DENSE GASES

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The equation of state for a gas of hard spheres is derived on the basis of the binary correlation function obtained by uncoupling the Bogolyubov chain.[1-3] The calculations are compared with the equation of state corresponding to the sum of seven terms of the virial series.[6] For $\rho = \pi/v \leq 1.25$ (v is the specific volume of the system) both methods yield identical results with an accuracy to 5%.

As is well known, in gases and in liquids, thermal motion tends to distribute the matter uniformly over the entire volume of the system, as a result of which the gas molecules are separated for most of the time by distances close to the average distance $\bar{r}$. Therefore, if a sphere of radius equal to the correlation radius r_c is drawn around the molecule, then when $r_c < \bar{r}$ the probability that one "extraneous" molecule will fall inside this sphere is larger than the probability of finding in this sphere two "extraneous" molecules, etc. And if this is the case, then in the first approximation we can neglect all the correlations except the pair correlations; in the second approximation it is possible to take into account the triple correlations, leaving out the quadrupole correlations, etc. This idea was used in [1-3] to obtain from an infinite chain of Bogolyubov equations[4] a closed first-approximation equation for the binary distribution function G_{12}:

$$\nabla_1 g_{12} - \frac{1}{v}\int_v (1+g_{12}+g_{13}+g_{23})(1+f_{23})\nabla_1 f_{13} d^3r_3 = 0, \qquad (1)$$

where $G_{ij} = \gamma_{ij}(1 + g_{ij})$, $\gamma_{ij} = \exp[-\Phi_{ij}/\Theta]$, Φ_{ij} is the pair-interaction energy, $\Theta = kT$, $f_{ij} = \gamma_{ij} - 1$, and $v = V/N$. Equation (1) is of definite interest not only because it is the simplest in the theory of ordinary gases. It was shown in [2,5] that equation (1) can be used also to construct the theory of ionic systems in that range of parameters, where the Debye approximation is no longer applicable. This could not be done before with the aid of other, more complicated equations. Taking the foregoing into account, we have decided to investigate in greater detail the behavior of the solution of Eq. (1) for the simplest case of a gas of solid spheres, when

$$f(r) = \begin{cases} -1, & 0 < r < r_0 \\ 0, & r_0 \leqslant r \leqslant +\infty \end{cases}.$$

It is easy to show that in this case (1) takes the form (when $t \geq 1$)

$$g(t) = -\rho\int_{t-1}^{t+1} \frac{\tau[1-(t-\tau)^2]}{t}\gamma(\tau)g(\tau)\,d\tau$$
$$-\frac{\rho}{4}\int_t^{\infty}(\tau^2-4)f(\tau-1)g(\tau)\,d\tau - \rho\lambda f(t-1)[{}^1/_{12}t^3 - t + {}^4/_3], \qquad (2)$$

where $t = r/r_0$, $\rho = \pi r_0^3/v$, and $\lambda = 1 + g(1)$. If we seek the solution of this equation in the form

$$g(t) = \sum_{n=1}^{\infty}\rho^n g_n(t),$$

then we obtain for the equation of state $P = pv/\Theta$ the virial series $\sum_{n=1}^{\infty} B_n \rho^{n-1}$ in which, however, only the first three coefficients are exact; the remaining B_n differ greatly from the true values (see table I). Nonetheless, Eq. (2) makes it possible to obtain perfectly satisfactory results in the entire region[1)] $\rho \leq 1.25$. To prove this, we seek the solution of (2) in the form

$$g(t) = \lambda\sum_{n=1}^{\infty}\rho^n g_n(t).$$

Since $\lambda = 1 + g(1)$, we have

$$g(t) = \sum_{n=1}^{\infty}\rho^n g_n(t)\Big/\Big[1 - \sum_{n=1}^{\infty}\rho^n g_n(1)\Big]. \qquad (3)$$

Substituting this expression in the well known formula relating the pressure P with G(r), we get

$$P = \frac{pv}{\Theta} = 1 + \frac{2}{3}\rho\Big/\Big[1 - \sum_{n=1}^{\infty}\rho^n g_n(1)\Big]. \qquad (4)$$

The other expression for P can be obtained with the aid of the formula for the isothermal compressibility

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\Theta = \frac{v}{\Theta}\left\{1 - \frac{4\pi}{v}\int_0^\infty [G(r)-1]r^2\,dr\right\}. \qquad (5)$$

After elementary transformations we get

$$P_\beta = \frac{pv}{\Theta} = \frac{1}{\rho}\int_0^\rho\left\{1 - 4\rho\left[\frac{1}{3} - \sum_{n=1}^{\infty}\rho^n\int_1^\infty g_n(t)t^2\,dt\Big/\Big(1 - \sum_{n=1}^{\infty}\rho^n g_n(1)\Big)\right]\right\}^{-1} d\rho. \qquad (6)$$

It is obvious that in an internally self-consistent theory we should have $\delta_1 = (P - P_\beta)/P \equiv 0$.

Table I.

n	B_n Approximate values	B_n True values
1	1	1
2	$^2/_3$	$^2/_3$
3	$^5/_{18}$	$^5/_{18}$
4	$0.497\cdot10^{-1}$	$0.8502\cdot10^{-1}$
5	$0.704\cdot10^{-2}$	$0.2179\cdot10^{-1}$
6	$0.98\cdot10^{-2}$	$0.5083\cdot10^{-2}$
7	$0.2\cdot10^{-4}$	$0.1212\cdot10^{-2}$

1) We recall that the value $\rho \approx 1.2$ corresponds to the condition $r_c = \bar{r}$ for a system of hard spheres.

It can be shown that when $\rho \leq 0.75$ series (3)–(6) c converge absolutely; when $\rho > 0.75$ we can speak only of asymptotic convergence of the series, and the accuracy which is obtained thereby is much higher for (4) than for (5). The reason for the divergence of the series obviously lies in the fact that somewhere in the complex plane $\rho \exp i\varphi$, at $\rho \gtrsim 0.75$, there is located an "unphysical" pole. On the real ("physical") axis, Eq. (2) has no poles whatever in the vicinity of $\rho = 0.75$.

The proposed algorithm for solving (2) was realized with an electronic computer, and 12 terms of the series were calculated. Since the values of P_{2k-1} obtained while retaining an odd number of terms in the series are always larger than P_{2k} (see Table II), the true value $P = P_\infty$ lies somewhere at $P_{2k-1} \geq P \geq P_{2k}$. We therefore chose for P the value $P = (P_{2k-1} + P_{2k})/2$ at those values of the approximation number k, for which the difference $P_{2k-1} - P_{2k}$ was minimal. As seen from the data of Table II, when $\rho = 0.75$ the values of P_{2k-1} and P_{2k} vary monotonically with increasing k, whereas at $\rho = 0.875$ the growth of P_{2k} already gives way to a decrease at k = 6, thus indicating that the series has an asymptotic character. When $\rho = 1.00$ the difference $P_{2k-1} - P_{2k}$ begins to increase already at k = 3. The series for β converges at $\rho \leq 0.75$ and diverges at $\rho > 0.75$, without exhibiting an asymptotic behavior like the series for P.

In Table III are given the values of P and P_β, calculated from formulas (4) and (6). For comparison, the table indicates the values of the pressure P_7, calculated with the aid of a seven-term segment of the virial series,[6] as well as the value of P_{P-Y}, determined on the basis of the solution of the Percus–Yevick equation, obtained in [7]

$$P_{P\text{-}Y} = \frac{36 + 12\rho + 3\rho^2}{(6 - 0)^2} \qquad (7)$$

As seen from these data, the error $\delta = (P - P_7)/P_7$, with which the pressure is determined on the basis of Eq. (2), does not exceed 5% in the entire investigated interval, and the accuracy of Eq. (2) is even somewhat higher than the accuracy of the Percus–Yevick equation. The "non-self-consistency" parameter of Eq. (2) $\delta_1 = (P - P_\beta)/P$ is in this case also small. All this indicates that when the condition $r_c < \bar{r}$ is satisfied,

Table II.

k	ρ							
	0.750		0.875		1.000		1.250	
	P_{2k-1}	P_{2k}	P_{2k-1}	P_{2k}	P_{2k-1}	P_{2k}	P_{2k-1}	P_{2k}
1	1.7273	1.6860	1.9180	1.8434	2.1429	2.0150	2.7391	2.4030
2	1.7055	1.6946	1.8842	1.8573	2.0944	2.0346	2.6636	2.4198
3	1.7016	1.6966	1.8774	1.8608	2.0857	2.0373	2.6862	2.3805
4	1.7003	1.6974	1.8754	1.8619	2.0859	2.0351	2.7869	2.2895
5	1.6998	1.6978	1.8746	1.8623	2.0904	2.0293	3.0688	2.1254
6	1.6995	1.6980	1.8745	1.8622	2.0990	2.0196	4.1715	1.8777

Table III.

ρ	P_7	P	P_β	$\delta_1=(P-P_\beta)/P$, %	$P_{P\text{-}Y}$
0.125	1.0878	1.0878	1.0878	0.00	1.0878
0.250	1.1855	1.1852	1.1853	0.01	1.1853
0.375	1.2944	1.2938	1.2924	0.08	1.2936
0.500	1.4149	1.4138	$1.4075 \pm 2\cdot10^{-4}$	0.4	1.4132
0.625	1.5498	1.5481	$1.5250 \pm 5\cdot10^{-3}$	1.5	1.5462
0.750	1.7004	$1.6990 \pm 5\cdot10^{-4}$	$1.6500 \pm 6\cdot10^{-2}$	3.0 (?)	1.6942
0.875	1.8689	$1.8680 \pm 5\cdot10^{-3}$	—	—	1.8579
1.000	2.0575	$2.0590 \pm 2\cdot10^{-2}$	—	—	2.0400
1.125	2.2743	$2.2840 \pm 6\cdot10^{-2}$	—	—	2.2426
1.250	2.5067	$2.5420 \pm 1\cdot10^{-1}$	—	—	2.4681

which in this case is equivalent to the condition $\rho \lesssim 1.2$, Eq. (1), obtained by cutting off the Bogolyubov chain, actually leads to perfectly satisfactory results.

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