SOLUTION OF THE PERCUS-YEVICK EQUATIONS AND THERMODYNAMIC FUNCTIONS OF A DENSE GAS AT SUBCRITICAL TEMPERATURES

A. M. Berezhkovskii, N. M. Kuznetsov,
and I. V. Fryazinov

UDC 536.71

The solution of the Percus-Yevick equation [1] for a Lennard-Jones potential

$$U = 4\varepsilon\,[(a/r)^{12} - (a/r)^{6}] \tag{0.1}$$

and for other powers in the repulsive potential is obtained. The calculations with the Lennard-Jones potential were performed in the density interval $0.048 < n^* < 1.5$ for temperatures $T^* \geq 1.2$. The density and temperature are expressed here in dimensionless units:

$$n^* = na^3,\quad T^* = T/\varepsilon$$

where n is the number of particles in unit volume. The results are presented in tables expressing the dependence of energy and pressure on temperature and density. A transition of the solution to the high-temperature asymptotic approximation of Rowlinson [2, 3] is considered, and the applicability limits of the numerical results obtained are discussed for high density.

One of the contemporary theoretical methods of determining the equation of state of dense media, in which only data of the intermolecular potential are used as input data, is based on approximate solutions of integral equations for the radial distribution function g. The Percus-Yevick and the so-called approximate hypernetted chain equations lead to most satisfactory results in the sense of agreement with experimental data and with direct computer calculations of the statistical sums of simplest gases and liquids.

The Percus-Yevick equation was solved numerically in a number of papers [4-12] for other values of temperature and density and for any potential model. These calculations refer mainly to temperatures close to the critical and do not cover the whole region of thermodynamic parameters which is of practical interest.

1. Numerical Solution. The Percus-Yevick equation [7] can be represented in the form

$$\begin{gathered}
P(x) = 1 + \frac{2\pi n^*}{x}\int\limits_{\Delta} H(s)\,C(t)\,ds\,dt \\
x = r/a, \qquad \psi = 4\,(x^{-12} - x^{-6}) \\
P(x) = g(x)\exp\psi \\
C(x) = x\,P(x)\exp(-\psi - 1) \\
H(x) = x[P(x)\exp(-\psi) - 1]
\end{gathered} \tag{1.1}$$

For each fixed x the integration is over the semiinfinite band $\Delta = \Delta(x)$ bounded by the straight lines

$$s = t \pm x,\quad s = -t + x,\quad s > 0,\quad t > 0$$

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 2, pp. 111-118, March-April, 1972. Original article submitted August 2, 1971.

TABLE 1

T^*	$n^* \cdot 10^4$													
	1440	1728	2074	2488	2986	3583	4300	5160	6192	7430	8916	10699	12839	15407
1.2	506	425	344	278	225	187	191	322	768	1912	4541	10330*	23070*	—
1.4	646	593	538	487	447	431	473	648	1119	2223	4651	9863*	21140*	—
1.6	737	699	662	630	610	619	690	894	1379	2449	4722	9496*	19650*	—
1.8	804	778	755	738	735	765	858	1084	1578	2617	4765	9192*	—	—
2.0	856	840	827	822	835	880	992	1233	1732	2746	4789	8932*	17510*	—
2.2	897	889	885	890	915	974	1100	1353	1855	2844	4800	8706*	16690*	—
2.4	931	929	932	946	980	1051	1188	1451	1954	2921	4800	8504*	16000*	—
2.7	971	976	989	1013	1059	1143	1293	1566	2069	3007	4788	8238	15110*	—
3.0	1002	1013	1033	1065	1121	1214	1374	1655	2155	3066	4765	8005	14380*	—
3.3	1027	1043	1068	1107	1170	1271	1439	1724	2220	3108	4735	7800	13760*	25840*
3.6	1048	1067	1097	1141	1209	1317	1490	1779	2271	3137	4703	7617	13220*	24480*
4.0	1069	1093	1128	1177	1252	1366	1545	1836	2322	3162	4657	7400	12610*	22960*
5.0	1107	1138	1180	1239	1323	1447	1635	1927	2398	3184	4540	6960	11450*	20130*
6.0	1130	1165	1212	1277	1367	1496	1686	1976	2432	3175	4428	6618	10600*	18160*
8.0	1155	1195	1247	1317	1413	1546	1737	2018	2447	3124	4230	6106	9417	15520*
10.0	1168	1210	1265	1337	1434	1567	1755	2027	2434	3062	4067	5736	8619	13820*
14.0	1179	1223	1279	1351	1448	1578	1759	2014	2387	2946	3817	5222	7578	11700*

TABLE 2

T^*	$n^* \cdot 10^4$													
	1440	1728	2074	2488	2986	3583	4300	5160	6192	7430	8916	10699	12839	15407
1.2	470	246	—12	—254	—479	—726	—1042	—1465	—2005	—2643	—3293	—3704*	—3190*	—
1.4	719	571	400	203	—20	—279	—590	—971	—1434	—1963	—2485	—2782*	—2259*	—
1.6	857	735	592	425	230	—1	—278	—612	—1010	—1456	—1883	—2095*	—1567*	—
1.8	952	848	724	578	406	201	—44	—338	—683	—1063	—1417	—1564*	—	—
2.0	1023	932	823	694	540	358	139	—120	—423	—751	—1046	—1142*	—613*	—
2.2	1078	997	900	784	647	483	287	56	—211	—497	—744	—800*	—273*	—
2.4	1123	1049	962	858	733	585	409	201	—36	—286	—494	—517*	+6*	—
2.7	1175	1111	1035	945	837	709	556	378	177	—29	—191	—175	+342*	—
3.0	1215	1160	1093	1013	919	806	673	518	346	+174	+49	+94	604*	—
3.3	1248	1198	1139	1068	984	885	767	632	484	339	244	312	814*	2417*
3.6	1274	1230	1177	1114	1039	950	845	726	598	476	405	491	986*	2501*
4.0	1303	1264	1218	1163	1097	1020	931	830	722	625	580	685	1171*	2587*
5.0	1353	1325	1290	1250	1202	1146	1083	1013	944	890	889	1025	1489*	2723*
6.0	1386	1364	1338	1307	1271	1229	1183	1134	1089	1063	1090	1243	1687	2793*
8.0	1426	1412	1396	1376	1355	1331	1305	1282	1266	1273	1330	1499	1909	2845*
10.0	1449	1440	1429	1417	1404	1390	1377	1368	1369	1393	1466	1640	2024	2850*
14.0	1476	1472	1467	1463	1459	1456	1457	1463	1482	1524	1610	1784	2129	2818*

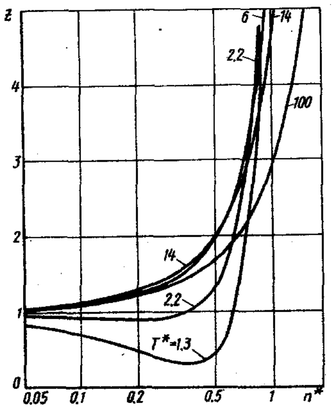

Fig. 1

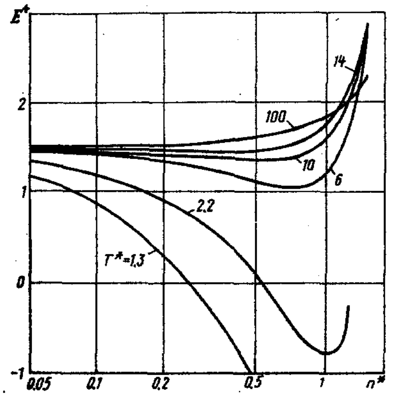

Fig. 2

On passing from the point $x+h$ this band is broadened by $\sqrt{2}\,h$ and "shortened" by $h/\sqrt{2}$. Thus, if the integral over the band $\Delta(x)$ in (1.1) is known, calculating the corresponding integral over the band $\Delta(x+h)$ is reduced to evaluating integrals over a band of width $h/\sqrt{2}$. Each of these integrals can be approximately replaced (for small h) by one-dimensional integrals and evaluated by the trapezoidal rule. At the same time the semiinfinite band Δx is replaced by a rectangle, formed by the straight lines mentioned above and by the line $s=-t+X$. We thus obtain a finite system of algebraic equations which can be solved for P(x) in a grid by Newton's method. The step of the grid was $h=0.05$, and $X=7$. For such values of h and X the order of the algebraic system of equations was 140. A check showed that for $h \leq 0.05$ and $X \geq 7$ the calculation of the radial distribution function and of the thermodynamic functions was independent of h and X within a relative error of 10^{-4}.

The densities are given by the geometric-progression equation

$$n_i^* = 0.1q^{i-5}, \quad q = 1.2, \quad i = 1,2,\ldots,20$$

For given values of density n_{i+1}^* and temperature T^* we used as the zeroth iteration of the function P(x) the already-found solution at the neighboring point n_i^* on the same isotherm T^*. At the lowest-density point the zeroth iteration was the corresponding solution for an ideal gas, i.e., $g=1$, $P(x)=\exp\psi$. At each iteration we calculated the compressibility coefficient $Z=p^*/(n^*T^*)$ and the particle energy divided by temperature $E^+=E^*/T^*$. Here p^* and E^* are the dimensionless pressure and energy, related to the corresponding dimensional quantities by

$$p^* = pa^3/\varepsilon, \qquad E^* = E/\varepsilon$$

The quantities Z and E^+ were calculated by the equations

$$Z = 1 - \frac{2\pi n^*}{3T^*}\int_0^\infty \frac{d\psi}{dx}\, g(x)\, x^3 dx$$

$$E^+ = \frac{3}{2} + \frac{2\pi n^*}{T^*}\int_0^\infty \psi g(x)\, x^2 dx$$

In these equations, for $x=X=7$ we assumed $g=1$. The calculation of Z and E^+ does not depend, within the accuracy limits of $\Delta Z/Z = \Delta E^+/E^+ = 10^{-3}$, on a variation of X, if $X \geq 7$ (see also [10]). The iteration process was terminated when the relative difference in Z and E^+ in one iteration was less than 10^{-4}. The number of iterations necessary to achieve the given accuracy gradually increases with increasing density and with decreasing temperature. At the highest densities for which the calculation was still performed ($n^* \approx 1.5$ or $n^* \approx 1.3$ depending on temperature) the convergence of iterations was quite slow. These points are, obviously, close to the convergence limit of the iterational process.

The results of calculating $10^3 \cdot Z$ and $10^3 \cdot E^+$ at $n^* \geq 0.144$ are given in Tables 1 and 2. For lower densities, Z and E^+ are given within 1% by the expressions

TABLE 3

n^*	T^*					
	6	8	10	12	14	100
0.048	30	19	14	13	11	2
0.100	56	30	31	16	21	1
0.144	77	52	39	31	26	2
0.207	97	64	47	45	32	2
0.249	106	68	51	41	36	2
0.299	108	71	50	42	37	4
0.358	106	66	48	41	35	4
0.430	94	57	42	33	30	6
0.516	67	36	27	21	23	8
0.619	9	3	4	9	13	9
0.743	−40	−39	−30	−15	−7	18
0.892	−120	−89	−62	−34	−15	32
1.070	−191	−131	−92	−52	−18	52
1.284	−236	−161	−89	−34	+6	100
1.541	−221	−107	−18	+53	111	180

$$Z = 1 + {}^2/_3\pi n^* B^* + ({}^2/_3\pi n^*)^2 C^*$$
$$E^+ = {}^3/_2 - {}^2/_3\pi n^* (dB^* / d\ln T^* + {}^1/_3\pi n^* dC^* / d\ln T^*) \tag{1.2}$$

Here B^* and C^* are the reduced second and third virial coefficients [13] for the potential (0.1). To calculate Z and E^+ with an error less than 1% at any point in the region of thermodynamic parameters covered by the tables (excluding their last three columns), it is sufficient to interpolate through three or four nearest reference points.

The two-dimensional Table 1 together with Eqs. (1.2) contains the total information about thermodynamic functions of the system of particles considered here, not possessing internal degrees of freedom. For example, the reduced free energy $F^* = F/\varepsilon$ can be calculated from

$$F^* = NT^* \int_0^{n^*} [Z(t, T^*) - 1]\, t^{-1} dt + F_0/\varepsilon$$

Here F_0 is the free energy of an ideal gas, and N is the number of particles.

2. Discussion of Results. Comparison with the Rowlinson Asymptotic Approximation. As could be expected, at low densities the pressure and energy are close to those of an ideal gas ($Z \approx 1$, $E^+ \approx {}^3/_2$). At increasing densities and low temperatures the role of attractive forces increases, and Z and E^+ decrease. At still higher densities and temperatures the nonideality of the gas is mostly connected with the repulsive part of the potential, and then $Z > 1$ and $E^+ > {}^3/_2$. The general temperature and density dependence of the thermodynamic functions is illustrated in Figs. 1 and 2.

We notice that in the overlap region with the data in Tables 1 and 2 the values of Z and E^+ are in good agreement with calculations by Watts [10] and other authors.

Rowlinson showed [2, 3] that at sufficiently high temperatures molecules with a Lennard-Jones potential (0.1) can be considered as solid spheres whose diameter d depends on temperature as follows:

$$d = a(4/T^*)^{1/12}[1 + \Phi(T^*)/12] \tag{2.1}$$

The function $\Phi(T^*)$ varies monotonically from −3.571 to 0.577 for T^* varying from 2 to ∞. A detailed table of $\Phi(T^*)$ is given in [14]. Having evaluated the effective diameter, one can use the equation of state of solid spheres, obtained in [5] (see also [16]). This equation is of the form

$$Z = \frac{1 + y + y^2 - y^3}{(1 - y)^3}, \quad y = \frac{1}{6}\pi n^* \left(\frac{d}{a}\right)^3 \tag{2.2}$$

Rowlinson points out $T^* = 12$ as the lowest temperature at which the approximation (2.1) is valid. This limit, however, does not reflect the sensitivity of the approximations (2.1), (2.2) to density. For a more definite idea about the accuracy of the high-temperature asymptotic approximation and about the limit beyond which the solution of Eq. (1.1) becomes too difficult one can use the simpler equations of state (2.1), (2.2). Table 3 shows the difference $10^3(Z_2 - Z_1)/Z_1$, where Z_1 and Z_2 are the data of Table 1 and the calculations by Eqs. (2.1), (2.2), respectively. The comparison shows, in particular, that the pressure calculated in the Rowlinson approximation agrees with the Percus-Yevick calculations within less than 10% for $T^* > 10$ and $n^* < 1$.

As noticed, the maximum tabulated value of the density $n^*_{\max}$ is restricted by the convergence rate of the iteration. Already at pressures larger than (0.7-0.8) $n^*_{\max}$, however, the Percus-Yevick equation leads to unlikely results. This is seen by analyzing the density dependence of the coefficient $\gamma = \partial(ZT^*)/\partial T$. The values of γ, calculated by the data of Table 1, increase monotonically for increasing densities, reaching 8-10 for the last two lines of the table at low temperatures. As is not hard to show, in the high-density limit and for Lennard-Jones interactions, γ is independent of density and is expressed as follows in terms of the power of the potential: $\gamma = (m+2)/2$. For $m = 12$ we obtain $\gamma = 7$. From available experimental data on liquid and solid compressibilities at high pressures it also follows that γ usually does not exceed 6 and depends on density rather weakly.

TABLE 4

η	$\varphi(\eta)$	η	$\varphi(\eta)$
92.8	1.040	12.5	1.343
77.2	1.048	10.4	1.426
64.4	1.058	8.8	1.521
53.6	1.070	7.35	1.655
44.7	1.085	6.12	1.832
37.2	1.103	5.11	2.068
31.0	1.125	4.25	2.389
25.9	1.151	3.55	2.835
21.6	1.185	2.96	3.471
18.0	1.227	2.46	4.401
14.9	1.278	2.05	5.806

In view of these considerations it seems that at high densities and low temperatures, in the region where the Percus-Yevick equation leads to $\gamma > 6$, it is not of practical interest and is a too coarse approximation to statistical properties. The values of Z and E in the region $\gamma > 6$ in Tables 1 and 2 are marked by asterisks.

3. A Repulsive Power Potential. One of the simplest potential models, leading to a qualitatively correct thermodynamic description of a real gas at high temperatures ($T^* \gg 1$), is the repulsive power potential

$$U = 4\varepsilon / x^m \tag{3.1}$$

The expressions in dimensionless variables of the thermodynamic functions of the system whose particles interact according to (3.1) depend only on one variable [17]:

$$\eta = (T^*)^{3/m} / n^*$$

In particular

$$Z = \varphi_m(\eta)$$

$$E^+ = 3\left(\frac{1}{2} - \frac{1}{m}\right) + \frac{3}{m}\varphi_m(\eta)$$

Here $\varphi_m(\eta)$ is an unknown function of η, depending also on the potential parameter m.

The functions $\varphi_m(\eta)$ can be found by solving the Percus-Yevick equation. In this work this was done for $m = 12$. The results of the calculations are given in Table 4. The highest density and lowest temperature for which Eq. (1.1) leads to anomalously large γ (see Sec. 2) correspond to values of η smaller than unity. Such values of η are at the limit of the η region for which Table 4 was constructed.

In conclusion we notice that the calculations of thermodynamic functions at the selected potential parameters ε and a are directly applicable to monatomic media. After additional account of internal degrees of freedom, however, these results can also be applied to other substances with molecules possessing sufficiently high symmetry of valence shells and not undergoing significant change in structure in the transition from gas to condensed phases, such as N_2, O_2, H_2, and CH_4.

LITERATURE CITED

1. J. K. Percus and J. Yevick, "Analysis of classical statistical mechanics by means of collective coordinates," Phys. Rev., 110, No. 11 (1958).
2. J. S. Rowlinson, "An equation of state of gases at high temperatures and densities," Mol. Phys., 7, No. 4 (1964).
3. J. S. Rowlinson, "The statistical mechanics of systems with steep intermolecular potentials," Mol. Phys., 8, No. 2 (1964).
4. A. Broyles, S. U. Chung, and H. L. Sahlin, "Comparison of radial distribution functions from integral equations and Monte Carlo," J. Chem. Phys., 37, No. 10 (1962).
5. A. A. Khan, "Radial distribution functions of fluid argon," Phys. Rev., 134, No. 2A (1964).
6. A. A. Khan, "Radial distribution functions of liquid krypton," Phys. Rev., 136, No. 5A (1964).
7. A. A. Khan and A. A. Broyles, "Interatomic potentials and x-ray-diffraction intensities for liquid xenon," J. Chem. Phys., 43, No. 1 (1965).
8. D. Levesque, "Percus-Yevick, hyperchain, and Born-Green equations for a classical fluid," Physica, 32, No. 11, 12 (1966).
9. G. J. Throop and R. J. Bearman, "The pair correlation function and thermodynamic properties of the Lennard-Jones 6-12 potential and the Percus-Yevick equation," Physica, 32, No. 7 (1966).
10. R. O. Watts, "Percus-Yevick equation applied to Lennard-Jones fluid," J. Chem. Phys., 48, No. 1 (1968).

11. J. C. Cure and S. E. Babl, "Percus-Yevick isotherm for the exp-6 intermolecular potential," J. Chem. Phys., 48, No. 5 (1968).
12. F. Mandel, R. J. Bearman, and M. Y. Bearman, "Numerical solution of the Percus-Yevick equation for the Lennard-Jones 6-12 and hard sphere potentials," J. Chem. Phys., 52, No. 7 (1970).
13. J. Hirschfelder, C. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Chapman and Hall (1954).
14. R. Chen, D. Henderson, and S. Davison, "Quantum corrections to the equation of state of gases at high temperatures and densities," Proc. Nat. Acad. Sci. U. S., 54, No. 6 (1965).
15. N. F. Carnahan and K. E. Starling, "Equation of state for nonattracting rigid spheres," J. Chem. Phys., 51, No. 2 (1969).
16. N. F. Carnahan and K. E. Starling, "Thermodynamic properties of a rigid sphere fluid," J. Chem. Phys., 53, No. 2 (1970).
17. L. D. Landau and E. M. Lifshits, Statistical Physics, Pergamon Press (1969).