

VIRIAL EXPANSION FOR NON-IDEAL REFERENCE SYSTEM. III. CHAIN APPROXIMATIONS

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On the basis of the renormalized virial expansion, formulated in the preceding parts of this work, the renormalized one-chain approximation is constructed for the Helmholtz free energy and for the radial distribution function. Preliminary numerical results are presented for the system of particles interacting through the Lennard-Jones potential and for the hard-sphere reference system. The hard-sphere equation of state of Carnahan and Starling and the zeroth approximation for the hard-sphere radial distribution function ($g_0^0(r) = 0$ for $r < d$, $g_0^0(r) = 1$ for $r > d$, $d =$ hard-sphere diameter) are used in computations. The results are compared with the experimental data for argon. A good agreement of the critical temperature ($T_c^+ = 1.254$ vs experimental value 1.26 for argon, in reduced units), and relatively good agreement of the critical density (about 7% of discrepancy) are found. However, the calculated critical pressure differs significantly from the experimental value.

In the first two parts of this work [1] (hereafter referred to as I, II), the renormalized — for the non-ideal reference system — virial expansion of the Helmholtz free energy, A , and of the s -particle distribution functions $n_s(r^s)$, has been formulated, and its relations with the Zwanzig perturbation theory [2] have been discussed. In this part we shall discuss the possibilities of constructing some formal approximations, for which the graphical representation of the renormalized virial expansion forms a suitable starting point.

The simplest of such approximations is perhaps the ring, or one chain (OC) approximation, used mainly for describing the classical electron gas (*cf. e. g.* [3, 4]). Recently we have shown [5] that the OC approximation also qualitatively describes some aspects of first-order phase transitions and of condensed phases. We shall now construct the renormalized OC formulae, taking into account the properties of the reference system (ROC approximation). We shall also present preliminary numerical results obtained for the hard-sphere reference system and for the Lennard-Jones potential.

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The considered system and all notation are the same as in I and II. Especially, the subscript or superscript 0 will denote the reference system; v is the volume per particle, T — temperature, $W(r) = V(r) - V^0(r)$, where $V(r)$ and $V^0(r)$ are the true and reference intermolecular potentials.

1. General approximations

In this Section we shall consider some general properties of the renormalized virial expansion. The simplest way of introducing of the properties of the non-ideal reference system into any known approximate relation describing the free energy of a fluid under consideration, obtainable from the virial expansion, is the use of the formula (I.3.4) together with (I.3.3). Let $A_{id}^{(a)}$ denote the considered approximate expression for the free energy, obtained in the usual way, with the use of the exact intermolecular potential (*i. e.* with the ideal gas reference system); hence, the formulae (I.3.4) and (I.3.3) imply that

$$A_{id}^{(a)} \rightarrow A_r^{(a)} = A_0 + A_{id}^{(a)} - A_0^{(a)}, \quad (1.1)$$

where A_0 and $A_0^{(a)}$ are the exact and the approximate, free energy of the reference system respectively (the latter calculated in the same approximation as $A_{id}^{(a)}$), and $A_r^{(a)}$ is the desired approximation for the free energy, with the properties on the non-ideal reference system taken into account.

Note that (1.1) may be written down by intuitive reasoning: a given approximate expression for the free energy should be corrected by adding the difference between the exact and approximate free energy of the reference system. The appropriate relation for the radial distribution function:

$$g_r^{(a)}(r) = g_{id}^{(a)}(r) + e^{-W(r)/kT} [g_0(r) - g_0^{(a)}(r)], \quad (1.2a)$$

or

$$g_r^{(a)}(r) = g_{id}^{(a)}(r)g_0(r)/g_0^{(a)}(r), \quad (1.2b)$$

is implied by the formulae (I.4.1), (I.4.5) and (I.2.7), or by (I.4.4) and (I.2.10). Similar formulae may be easily written down for remaining distribution and correlation functions.

In the renormalized virial expansion, formulated in I, the subsequent terms are expressed by the contributions from linear graphs (built from two kinds of lines), multiplied by some rather involved combinations of the s -particle correlation functions of the reference system. The s -particle correlation functions (for $s \geq 3$) are usually unknown for non-ideal systems; besides, their presence in the integrals expressing renormalized virial coefficients leads to serious difficulties in formal summations of the virial series. We introduce thus, as is frequently done in similar situations, the superposition approximation for s -particle distribution functions $n_s^0(r^s)$ [6, 7]:

$$n_s^0(r^s) = v^{-s} \prod_{j>i=1}^s g^0(r_{ij}),$$

i. e.,

$$N_s^0 \equiv 1, \quad G_s^0 \equiv 1, \quad h_s^0 \equiv 0, \quad \text{for } s \geq 3 \quad (1.3)$$

(cf. I, Section 2). Another possibility would be to use the convolution approximation [7]; it is now an open question which of these two approximations is better.

The superposition approximation results in a remarkable simplification of the renormalized virial series: it is easy to convince oneself that all terms represented by graphs which are not doubly linked vanish identically when (1.3) is used. The renormalized virial series (of any quantity: A , n_s , $g(r)$, h_s , etc.) will be now of the same form as the usual Ursell-Mayer-Montroll [8] virial series. The only difference is that the renormalized graphs are built from two kinds of lines, representing the renormalized Mayer functions F_0 and F^1 (cf. Eq. (1.3.6)) in such a way that to every point of the graph at least one F^1 -line is attached. This very close resemblance — in the superposition approximation — of the renormalized virial series to the usual one will enable us to formulate — in the next Section — the renormalized one-chain approximation.

2. One-chain summations

One-chain (OC) approximation consists in an approximation of the m -th virial coefficient by the simplest (topologically) graph representing this coefficient. In the case of the free energy such a graph is a polygon (with m angles); for a radial distribution function it is one simple chain connecting two root points through m internal points. The whole virial series approximated in this manner may be easily summed up to the closed formulae. In the case of renormalized virial series (in the superposition approximation), because of the presence of two kinds of lines, we have more than one polygon (or simple chain) in every virial coefficient. This fact enables us to introduce at least two different OC approximations. The simplest one is to retain — for every virial coefficient — only that OC graph (polygon or simple chain) which is built from F^1 -lines only. Because in this case all lines in the retained graphs are identical, we have exactly the same topological situation as in [5]. All the calculations are thus identical as for the non-renormalized case (except that the original Mayer function $f(r)$ is now replaced by $F^1(r)$), and we get

$$A = A_0 - \frac{kT}{2v} \Gamma_1(0) + \frac{vkT}{2(2\pi)^3} \int dq \left\{ \ln \left| 1 - \frac{1}{v} \Gamma_1(q) \right| + \frac{1}{v} \Gamma_1(q) + \frac{1}{2v^2} \Gamma_1^2(q) \right\}, \quad (2.1)$$

$$g(r) = g^0(r) \exp \left\{ -\frac{W(r)}{kT} + \frac{1}{(2\pi)^3} \int dq e^{-iq \cdot r} \frac{\Gamma_1^2(q)}{v - \Gamma_1(q)} \right\}, \quad (2.2)$$

where

$$\Gamma_1(q) = \int dr e^{-iq \cdot r} F^1(r). \quad (2.3)$$

The pressure P (equation of state) is obtained by the differentiation of (2.1) with respect to v (it is to be noted that $\Gamma_1(q)$ depends on v through the radial distribution function of

the reference system):

$$P = - \left(\frac{\partial A}{\partial v} \right)_T = P_0 - \frac{kT}{2v} \left[\frac{1}{v} \Gamma_1(0) - G_1(0) \right] - \frac{kT}{2(2\pi)^3} \int d\mathbf{q} \left\{ \ln \left| 1 - \frac{1}{v} \Gamma_1(\mathbf{q}) \right| + \frac{\Gamma_1(\mathbf{q})}{v} \frac{v - G_1(\mathbf{q}) \Gamma_1(\mathbf{q})}{v - \Gamma_1(\mathbf{q})} - \frac{\Gamma_1(\mathbf{q})}{2v^2} \right\}, \quad (2.4)$$

where

$$G_1(\mathbf{q}) = \left[\frac{\partial}{\partial v} \Gamma_1(\mathbf{q}) \right]_T = \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} f^1(\mathbf{r}) \left[\frac{\partial}{\partial v} g^0(\mathbf{r}) \right]_T. \quad (2.5)$$

Another, and perhaps better, OC approximation (which will be called hereafter the renormalized OC-ROC — approximation) is constructed by retaining all the polygons or simple chains containing both F^1 and F^0 -lines. The presence of F^0 -lines, together with the rule that to every point at least one F^1 -line must be attached, complicates somewhat the summations. Let us first consider the summation of polygons (rings) of the free energy. Such a ring may contain sequences (chains) of any length of F^1 -lines, whereas the F^0 -lines cannot be linked with each other and must be separated by at least one F^1 -line. We shall thus proceed as follows:

The whole class $\{R\}$ of polygons describing the ROC approximation is divided into subclasses $\{R_k\}$, each containing rings with k F^0 -lines, and any number $(m-k) \geq k$ of F^1 -lines ($m \geq 3$ is the total number of lines = total number of points of the ring). The points to which F^0 -lines are attached will be called 0-points (there are $2k$ 0-points in the graph R_k).

Let us consider first the case $k = 1$. The m points of such a ring may be labeled in $m!/2$ topologically different ways (the graph possesses symmetry only with respect to left-right inversion), and the contribution to the free energy from the subclass $\{R_1\}$ is, from (I.3.7)–(I.3.10), and (1.3):

$$\begin{aligned} -kT \sum_{m=3}^{\infty} v^{-m+1} \frac{m!}{2} \lim_{V \rightarrow \infty} \frac{1}{V} \frac{1}{m!} \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_m F_{12}^0 F_{23}^1 \dots F_{m1}^1 = \\ = - \frac{kT}{2(2\pi)^3} \int d\mathbf{q} \sum_{m=3}^{\infty} v^{-m+1} \Gamma_0(\mathbf{q}) \Gamma_1^{m-1}(\mathbf{q}) = \\ = - \frac{kT}{2(2\pi)^3 v} \int d\mathbf{q} \Gamma_0(\mathbf{q}) \frac{\Gamma_1^2(\mathbf{q})}{v - \Gamma_1(\mathbf{q})}, \end{aligned} \quad (2.6)$$

where

$$\Gamma_0(\mathbf{q}) = \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} F^0(\mathbf{r}). \quad (2.7)$$

$\Gamma_1(\mathbf{q})$ is given by (2.3), and the well-known properties of the Fourier transforms of convolutions have been used.

When $k \geq 2$, we first choose $2k$ 0-points, and divide the remaining points into k groups, containing m_1, m_2, \dots, m_k points ($m_i \geq 1, 2k + \sum m_i = m$, the total number of points of the ring), each group of points belonging to one chain of F^1 -lines. This may be done in $m!/(2k)!m_1! \dots m_k!$ different ways. The m_i points within the i -th F^1 -chain may be labeled in $m_i!$ different ways. We now construct the generalized ring, built of $2k$ 0-points,

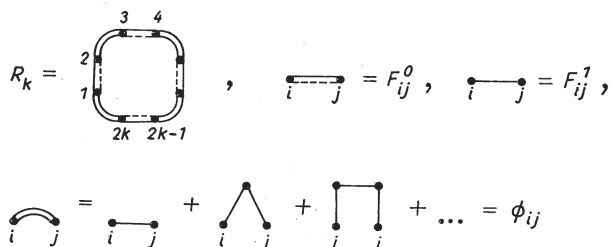


Fig. 1. Generalized ring R_k

by summing the contributions from all graphs which differ only in the number of points within a given F^1 -chain. The contribution to the free energy from the generalized ring, drawn in Fig. 1, is thus:

$$R_k = -kTv^{-2k+1} \frac{1}{(2k)!} \lim_{V \rightarrow \infty} \frac{1}{V} \int \dots \int dr_1 \dots dr_{2k} F_{12}^0 \Phi_{23} F_{34}^0 \dots \Phi_{2k,1}, \quad (2.8)$$

where

$$\Phi(r) = \frac{v}{(2\pi)^3} \int dq e^{-iq \cdot r} \frac{\Gamma_1(q)}{v - \Gamma_1(q)}. \quad (2.9)$$

The summation of all generalized rings is now easy: it is sufficient to note that such a ring possesses a k -fold symmetry axis (cf. Fig. 1), as well as symmetry with respect to the left-right inversion, so that the combinatorial factor for it is $(2k)!/2k$, and using (2.9) and (2.7), we get:

$$\begin{aligned} \sum_{k=2}^{\infty} \frac{(2k)!}{2k} R_k &= -kT \frac{v}{2(2\pi)^3} \int dq \sum_{k=2}^{\infty} \frac{1}{k} \left[\frac{1}{v} \frac{\Gamma_0(q)\Gamma_1(q)}{v - \Gamma_1(q)} \right]^k = \\ &= \frac{vkT}{2(2\pi)^3} \int dq \left\{ \ln \left| 1 - \frac{1}{v} \frac{\Gamma_0(q)\Gamma_1(q)}{v - \Gamma_1(q)} \right| + \frac{1}{v} \frac{\Gamma_0(q)\Gamma_1(q)}{v - \Gamma_1(q)} \right\}. \end{aligned} \quad (2.10)$$

The complete ROC approximation for the free energy is obtained by summing the contributions from all rings, including rings containing no F^0 -lines, *i. e.*, by adding together the contributions (2.1), (2.6), and (2.10):

$$\begin{aligned} A_{\text{ROC}} &= A_0 - \frac{kT}{2v} \Gamma_1(0) + \frac{vkT}{2(2\pi)^3} \int dq \left\{ \ln \left| 1 - \frac{1}{v} \Gamma_1(q) \left[1 + \frac{1}{v} \Gamma_0(q) \right] \right| + \right. \\ &\quad \left. + \frac{1}{v} \Gamma_1(q) \left[1 + \frac{1}{2v} \Gamma_1(q) + \frac{1}{v} \Gamma_0(q) \right] \right\}. \end{aligned} \quad (2.11)$$

The equation of state is thus:

$$\begin{aligned}
 P_{\text{ROC}} = P_0 - \frac{kT}{2v} \left[\frac{1}{v} \Gamma_1(0) - G_1(0) \right] - \frac{kT}{2(2\pi)^3} \int d\mathbf{q} \left\{ \ln \left| 1 - \frac{1}{v} \Gamma_1(q) \left[1 + \right. \right. \right. \\
 \left. \left. \left. + \frac{1}{v} \Gamma_0(q) \right] \right| + \frac{[\Gamma_1(q) - G_1(q)] [v + \Gamma_0(q)] + \Gamma_1(q) [\Gamma_0(q) - G_0(q)]}{v^2 - \Gamma_1(q) [v + \Gamma_0(q)]} + \right. \\
 \left. + \frac{G_1(q)}{v} [1 + \Gamma_1(q) + \Gamma_0(q)] + \frac{1}{v} \Gamma_1(q) \left[G_0(q) - \frac{\Gamma_0(q)}{v} - \frac{\Gamma_1(q)}{2v} \right] \right\}, \quad (2.12)
 \end{aligned}$$

where

$$G_0(q) = \left[\frac{\partial}{\partial v} \Gamma_0(q) \right]_T. \quad (2.13)$$

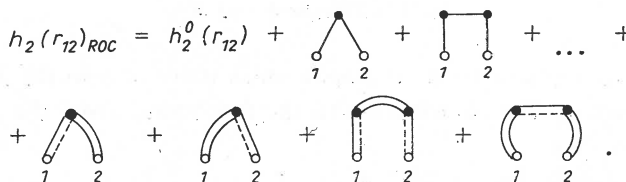


Fig. 2. Generalized one-chain graphs for the ROC approximation of the radial distribution function. The symbols are the same as in Fig. 1

The ROC approximation for the radial distribution function may be constructed in a similar way. The generalized graphs of $g_{\text{ROC}}(r)$ are shown in Fig. 2 (strictly speaking, these graphs represent the two-particle effective pseudopotential $h_2(r)$ — cf. I), and the result is

$$\begin{aligned}
 g_{\text{ROC}}(r) = g^0(r) \exp \left\{ - \frac{W(r)}{kT} + \right. \\
 \left. + \frac{1}{(2\pi)^3} \int d\mathbf{q} e^{-i\mathbf{q}\cdot\mathbf{r}} \frac{\Gamma_1^2(q) [v + \Gamma_0(q)] + \Gamma_1(q) \Gamma_0(q) [2v + \Gamma_0(q)]}{v^2 - \Gamma_1(q) [v + \Gamma_0(q)]} \right\}. \quad (2.14)
 \end{aligned}$$

3. Numerical results

We shall consider a system where the complete intermolecular potential is that of Lennard-Jones

$$v(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]. \quad (3.1)$$

As the reference system we choose a gas of hard spheres of diameter d :

$$V^0(r) = \begin{cases} \infty & r < d, \\ 0, & r > d \end{cases} f^0(r) = \begin{cases} -1 & r < d \\ 0 & r > d \end{cases}. \quad (3.2)$$

In this case the difference $W(r) = V(r) - V^0(r)$ has no meaning for $r < d$. We shall thus admit that the corresponding Mayer function is of the form

$$f^1(r) = \begin{cases} 0 & r < d \\ f(r) & r > d \end{cases}, \quad f(r) = e^{-V(r)/kT} - 1, \quad (3.3)$$

which means that we choose $W(r)$ as:

$$W(r) = \begin{cases} 0 & r < d \\ V(r) & r > d \end{cases}. \quad (3.3a)$$

The last relation is usually chosen when one deals with the hard-sphere reference system (cf., e. g., [9-11]). In order to take into account the fact that the Lennard-Jones potential is finite (although high) for finite $r < d$, Barker and Henderson [9] (cf. also [10]) proposed to calculate the hard-sphere diameter from the relation

$$d = d(T) = - \int_0^\sigma f(r) dr. \quad (3.4)$$

We shall adopt this proposition in our calculations; we shall also show how the change in d influences the results.

As the equation of state of the system of hard spheres we take that of Carnahan and Starling [12]:

$$\frac{P_0 v}{kT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3}, \quad y = \pi d^3 / 6v, \quad (3.5)$$

which implies

$$A_0 = A_{id} + kT \left[\frac{2}{1 - y} + \frac{1}{(1 - y)^2} \right], \quad (3.6)$$

where A_{id} is the ideal gas free energy per one particle.

The analytic form of the radial distribution function of the system of hard spheres, $g^0(r)$, is now also known [13] (cf. also [10]). Its use is, however, rather tedious because it requires numerical inversions of the Laplace transforms for every value of density. We shall thus use for the present — preliminary — calculations the zeroth approximation for $g^0(r)$:

$$g_0^0(r) = \begin{cases} 0 & r < d \\ 1 & r > d \end{cases}. \quad (3.7)$$

We shall express all the computed quantities in the following reduced units:

$$\begin{aligned} T^+ &= kT/\varepsilon, \quad V^+ = v/b_0, \quad P^+ = Pb_0/\varepsilon, \quad b_0 = \frac{2}{3}\pi\sigma^3, \quad d^+ = d/\sigma, \\ A^+ &= A/\varepsilon + T^+ \ln(b_0/\lambda^3), \quad i. e., \quad A_{id}^+ = -T^+[1 + \ln(V^+)], \end{aligned} \quad (3.8)$$

where λ is the thermal de Broglie wavelength (cf. I).

Computations were performed with the ODR-1204 computer; the Simpson rule was used for computing the integrals involved. It is to be noted that, within the parameter

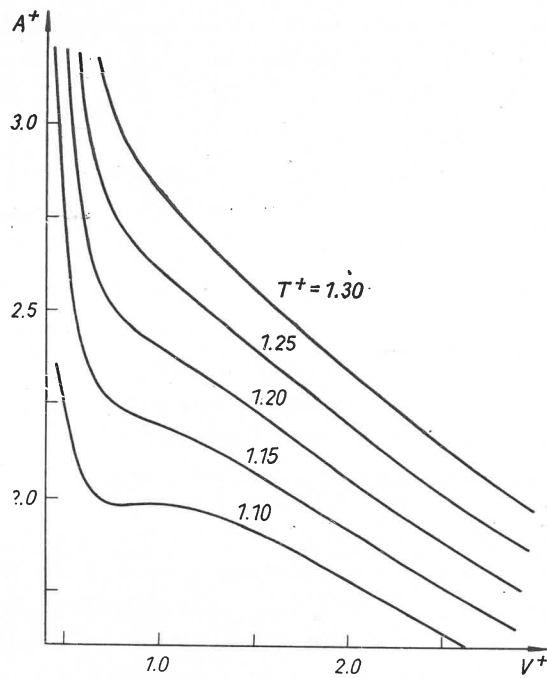


Fig. 3. The dependence of the free energy on specific volume in the ROC approximation. The curves are labeled by the values of temperature

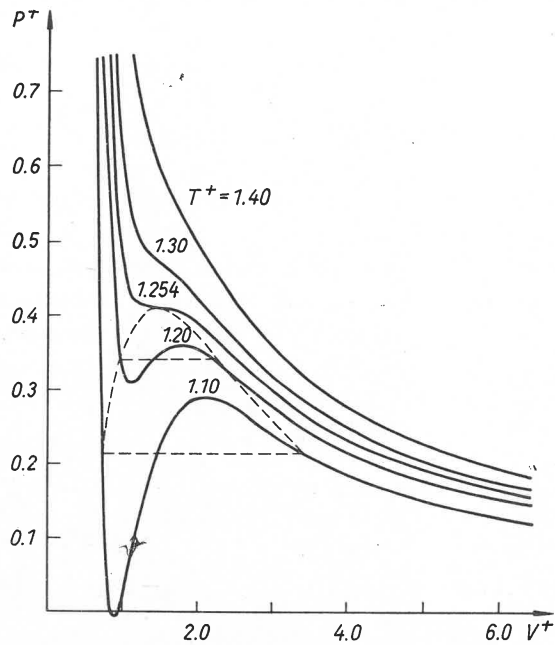


Fig. 4. Pressure-volume isotherms in the ROC approximation. The curves are labeled by the values of temperature

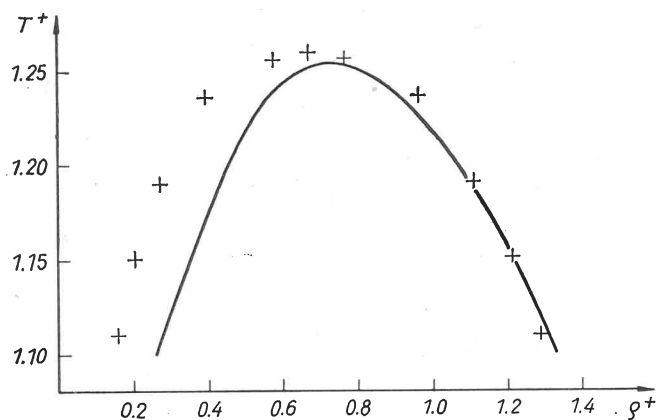


Fig. 5. Phase diagram for the gas-liquid transition in the ROC approximation (solid line). Crosses denote the experimental values for argon [15]

ranges used in this work, all integrands involved (including the logarithmic and rational functions in Eqs (2.11) and (2.12)) have no singular points.

The dependence of the free energy and pressure on volume in the ROC approximation, Eqs (2.11) and (2.12), is shown in Figs 3 and 4 for several temperatures. It is seen that these are van der Waals-like isotherms, which are interpreted in the usual manner (*cf.*, *e. g.*, [14]) as describing the gas-liquid phase transition and the critical point of this transition. The dashed lines in Fig. 4 show the regions of coexisting phases, determined from Fig. 3 together with the stability condition $(\partial^2 A/\partial v^2)_T > 0$. Figure 5 presents the phase diagram for the gas-liquid phase transition, *i. e.*, the densities $\rho^+ = 1/V^+$ of the coexisting phases *vs.* temperature T^+ , determined from Fig. 4 (full line), and the experimental values (crosses) for argon¹ [15]. A comparison of the values of T_c^+ , V_c^+ , and P_c^+ and compressibility $(Pv/kT)_c$ at the critical point, calculated in the ROC approximation, with the experimental values [14, 11], as well as with the values obtained from the perturbation equation of Barker and Henderson (BH) [9] and the perturbation-variation method of Mansoori and Canfield (MC) [11], is given in Table I.

TABLE I

Comparison of the critical constants

	Experimental [11]	BH [9,11]	MC [11]	ROC Eqs (2.11), (2.12)
T_c^+	1.26	1.35	1.36	1.254
V_c^+	1.50	1.59	1.47	1.40
P_c^+	0.248	0.293	0.346	0.411
$\frac{Pv}{kT_c}$	0.293	0.345	0.374	0.460

¹ In the reduction of experimental data the values of $\sigma = 3.405 \text{ \AA}$, $\epsilon/k = 119.8 \text{ }^\circ\text{K}$ [15, 11] have been used.

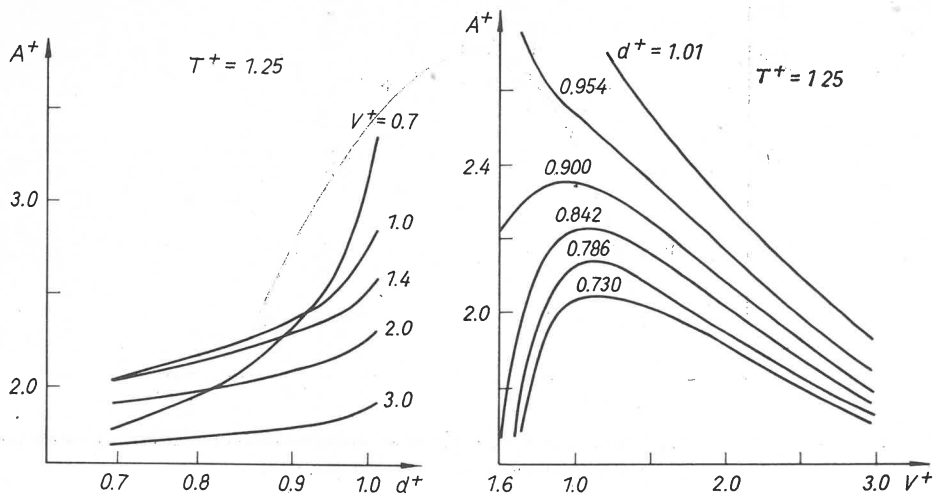


Fig. 6. The influence of the hard-sphere diameter on the values of the free energy calculated in the ROC approximation for $T^+ = 1.25$

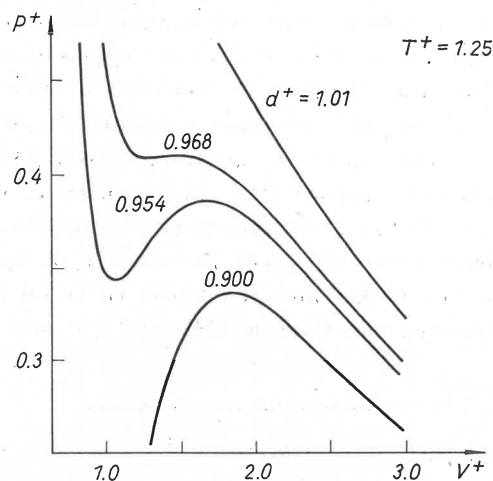


Fig. 7. The influence of the hard-sphere diameter on the values of the pressure calculated in the ROC approximation for $T^+ = 1.25$

All of the above results have been obtained for hard-sphere diameters d calculated from the Barker-Henderson prescription (3.4). We have also performed computations for different values of d in order to see how the assumed properties of the hard-sphere reference system influence the results obtained in the ROC approximation. Figures 6–8 show the dependence of the free energy, pressure and critical constants on the hard-sphere

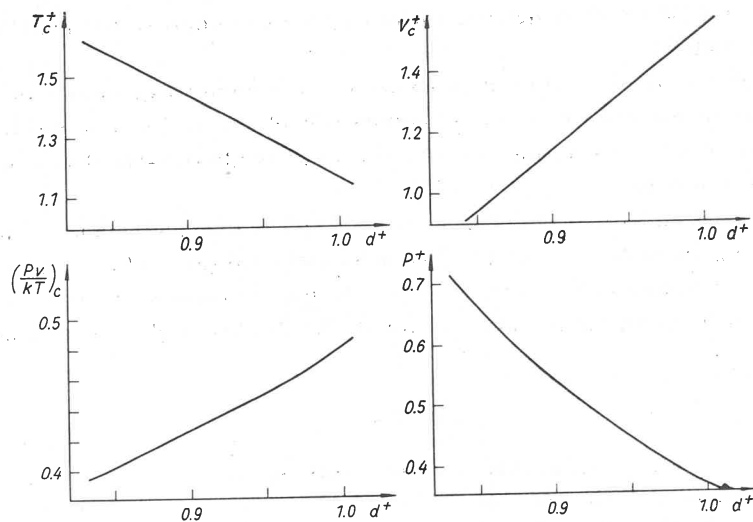


Fig. 8. The influence of the hard-sphere diameter on the values of the critical parameters calculated in ROC approximation.

diameter. It is seen that all these quantities depend fairly strongly on d^+ . It is noteworthy that d^+ calculated from the relation (3.4) does not change very much with temperature: from 0.973 for $T^+ = 1$ to 0.957 for $T^+ = 2$.

4. Final remarks

The preliminary numerical results presented in the preceding Section seem to show that the ROC approximation may provide a simple enough and reliable analytical equation of state for simple liquids. It is seen from Table I that the ROC approximation predicts the best value of the critical temperature and only a slightly worse value of the critical specific volume in comparison with the perturbation BH equation of state and the perturbation-variation MC method. On the other hand, the value of the critical pressure (hence, the critical compressibility $(Pv/kT)_c$ also) calculated from the ROC approximation is much too high. The phase diagram in Fig. 5 shows that the presented calculations lead to better results for the density of the liquid than of the gaseous phase. The BH and MC theories predict much better agreement with the experimental coexistence curve at lower temperatures, but much worse near the critical point (compare with Table I). The good agreement with the experimental values of the critical temperature and critical volume calculated in the ROC approximation is all the more interesting that we have used only the zeroth approximation, Eq. (3.7), for the radial distribution function of the hard-sphere reference system, whereas the BH and MC results are obtained with the use of the full (as far as possible) $g^0(r)$. Moreover, the use of the zeroth approximation, $g_0^0(r)$, in the BH or MC formulae leads to completely erroneous results. It is, however, an open ques-

tion whether the use of more detailed forms of $g^0(r)$ will improve the predictions of the ROC approximation.

Figures 6–8 show the strong dependence of all computed quantities on the chosen value of the hard-sphere diameter d . The comparison of data collected in Fig. 8 and Table I seems to show that the best results are obtained when the Barker-Henderson relation (3.4) is used ($d^+ = 0.968$ for $T^+ = T_c^+ = 1.25$).

Figure 6 also shows that in our case the hard-sphere diameter cannot be used directly as the variational parameter: within the whole investigated range of d^+ , the free energy A^+ is a monotonic function of d^+ . This fact, however, may be connected, among other things, with the use of the zeroth approximation for the hard-sphere radial distribution function.

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