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CHARACTERISTICS OF THE P, ϱ, T SURFACES OF REAL FLUIDS IN THE REGION OF SOLID STATE DENSITIES

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Evidence is presented for representing the above-critical isothermal pressure density dependence of N_2, Xe and propylene fluids by rational functions, say $P(\varrho) = A(\varrho, \mathrm{m})/B(\varrho, n)$, where A and B are m-th and n-th order polynomials in ϱ such that

$$\partial^2 A/\partial\varrho^2 = \partial^4 A/\partial\varrho^4 = \partial^2 B/\partial\varrho^2 = \partial^4 B/\partial\varrho^4 = 0$$

when ϱ equals critical density ϱ_c and certain temperature independent density $\varrho_{cf} \in [3\varrho_c, 5\varrho_c]$. Such isothermal pressure-density representations display first order poles at $o = \varrho_{max} \in [4\varrho_c, 6\varrho_c]$, implying values for effective diameters of N_2 and Xe molecules in agreement with those obtained from effective potentials.

1. Introduction

Analysing experimental P, ϱ, T data of some real fluids by osculating functions we obtained results [1,2,3,4] which suggest that the isothermal P, ϱ dependences of real fluids are such that there are two characteristic densities:

i) temperature independent density $\varrho_{cc} \approx$ critical density ϱ_c, and

ii) possibly temperature dependent density $\varrho_{cf} \in [3\varrho_c, 7\varrho_c]$. In the vicinity of ϱ_{cc} the isothermal P, ϱ dependences of those real gases which have been considered have turned out to be well represented locally by the rational ansatz

$$P(\varrho, T, m, n) = A(\varrho, T, m)/B(\varrho, T, n), \tag{1}$$

where

$$A(\varrho, T, m) = RT\varrho + \sum_{i=2}^{m} A_i \varrho^i \tag{2}$$

and

$$B(\varrho, T, n) = 1 + \sum_{i=2}^{n} B_i \varrho^i \tag{3}$$

are such that

$$\frac{\partial^2 A}{\partial \varrho^2} = 0, \quad \frac{\partial^4 A}{\partial \varrho^4} = 0, \quad \frac{\partial^2 B}{\partial \varrho^2} = 0 \text{ and } \frac{\partial^4 B}{\partial \varrho^4} = 0 \tag{4}$$

at $\varrho = \varrho_{cc} \approx \varrho_c$. Furthermore, certain analytic extrapolations of the isothermal P, ϱ dependences of some real gases considered seem also to be well represented in the vicinity of $\varrho = \varrho_{cf}$ by ansatz (1) which satisfies conditions (4) at $\varrho = \varrho_{cc}$ and at $\varrho = \varrho_{cf}$. Now, condition (4) at $\varrho = \varrho_{cc} \approx \varrho_c$, being al local property of P, ϱ, T surfaces along the experimentally accesible density line $\varrho = \varrho_{cc}$, has been implied directly by experimental P, ϱ, T data, whereas relation (4) at $\varrho = \varrho_{cf}$, observed as the local property of certain extrapolated P, ϱ, T surfaces of real fluids in the region of solid state densities, has not been directly implied by experimental observation of isothermal P, ϱ dependences of real fluids.

The observed properties [1,2,3,4] of certain empirical equations of state for some real fluids suggest, however, the following hypothesis [4] which can be directly verified by experimental P, ϱ, T data: The physically proper analytic expression for representing sufficiently accurate experimental isothermal P, ϱ data of real fluids outside the critical region is the rational ansatz (1) which satisfies conditions (4) at $\varrho = \varrho_{cc} \approx \varrho_c$ and at some temperature independent solid state density $\varrho_{cf} \in [3\varrho_c, 7\varrho_c]$. It is the aim of this paper to provide the following evidence in support of this hypothesis:

i) In the case of the isothermal P, ϱ dependences of N_2, Xe and propylene fluids assumption (4) at $\varrho = \varrho_{cf}$, where ϱ_{cf} is a temperature independent solid state density, turns out to improve the fitability of some rational ansatzes (1) considered.

ii) Rational functions used for representing isothermal P, ϱ dependences of real fluids N_2, Xe and propylene tend to infinity as the density approaches a certain maximal density $\varrho_{max}(T) \in [4\varrho_c, 6\varrho_c]$, where they display a first order pole. Thereby they suggest that the fluids considered may be hard to compress beyond density ϱ_{max} due to the finite size of their molecules about which the values of ϱ_{max} imply qualitatively correct estimates.

2. *Test of the proposed hypothesis against experimental data*

In order to find arguments in support of the hypothesis proposed we will compare the fitability of two kinds of rational ansatzes (1, 2, 3), say of

$$P(\varrho, m, n, \varrho_{cf}, T) = A(\varrho, m, \varrho_{cf}, T)/B(\varrho, n, \varrho_{cf}, T) \tag{5}$$

such that polynomials A and B satisfy the following relations

$$\frac{\partial^2 A}{\partial \varrho^2} = \frac{\partial^4 A}{\partial \varrho^4} = \frac{\partial^2 B}{\partial \varrho^2} = \frac{\partial^4 B}{\partial \varrho^4} = 0 \tag{6}$$

at $\varrho = \varrho_c$ and at $\varrho = \varrho_{cf}$, and of an associated comparative ansatz

$$P^*(\varrho, m-2, n-2, T) = A^*(\varrho, m-2, T)/B^*(\varrho, n-2, T) \tag{7}$$

with polynomials A^* and B^* defined by (2, 3) being such that

$$\frac{\partial^2 A^*}{\partial \varrho^2} = \frac{\partial^4 A^*}{\partial \varrho^4} = \frac{\partial^2 B^*}{\partial \varrho^2} = \frac{\partial^4 B^*}{\partial \varrho^4} = 0 \tag{8}$$

only at $\varrho = \varrho_c$; further, they both incorporate the ideal gas law in the low density limit by satisfying relations

$$A(0, m, \varrho_{cf}, T) = 0,\ \partial A(\varrho = 0, m, \varrho_{cf}, T)/\partial \varrho = RT,\ B(0, n, \varrho_{cf}, T) = 1, \tag{9}$$

and

$$A^*(0, m-2, T) = 0,\ \partial A^*(\varrho = 0, m-2, T)/\partial \varrho = RT,\ B^*(0, n-2, T) = 1. \tag{10}$$

Now, ϱ_{cf} being a constant whose value is chosen in advance, both ansatzes have only $m + n - 9$ independently adjustable parameters. So for a given real fluid it makes sense to compare how they are able to fit P, ϱ dependences of different isotherms at various temperature independent values of ϱ_{cf}.

To do this, we proceed as follows:

i) We take N experimental P, ϱ values corresponding to an isotherm T, say P_i, ϱ_i, $i = 1, 2, \ldots, N$.

ii) For chosen values of m, n and ϱ_{cf} we determine parameters A_i's and B_i's of ansatz $P(\varrho, m, n, \varrho_{cf}, T)$ so that they minimize the weighted standard deviation, say

$$\Delta(m, n, \varrho_{cf}, T) = (N^{-1} \sum_{i=1}^{N} [P_i - P(\varrho_i, m, n, \varrho_{cf}, T]^2 P_i^{-2})^{1/2}; \tag{11}$$

we denote the optimal value obtained by $\Delta_{opt}(m, n, \varrho_{cf}, T)$.

iii) Analogously we determine the best possible fit of the isothermal experimental data P_i, ϱ_i, $i = 1, 2, \ldots, N$, by comparative ansatz $P^*(\varrho, m-2, n-2, T)$ and denote by $\Delta^*_{opt}(m-2, n-2, T)$ the optimal value of the weighted standard deviation defined in analogy to (11).

iv) We declare the reciprocal of the ratio

$$R(m, n, \varrho_{cf}, T) = \Delta_{opt}(m, n, \varrho_{cf}, T)/\Delta^*_{opt}(m-2, n-2, T) \tag{12}$$

as a quantitative measure of how much our assumption of relation (6) at a given value of ϱ_{cf} improves the fitability of a rational ansatz in the particular case considered. We calculate this ratio as a function of ϱ_{cf} looking for those values of ϱ_{cf} where this ratio supports the hypothesis proposed by having values smaller than one.

v) We repeat this procedure both for different ansatzes, i. e. for various values of m and n, as well as for different isotherms. Thereby we look for those values of ϱ_{cf} where $R(m, n, \varrho_{cf}, T) < 1$ for all considered values of m, n and T, because the validity of the hypothesis (6) at a »true« value of ϱ_{cf} does not depend on the temperature as the isotherm considered, and should be observable for several different ansatzes $P(\varrho, m, n, \varrho_{cf}, T)$. Let us notice that both m and n should be greater than or equal to six if we wish to avoid considering ansatzes $P(\varrho, m, n, \varrho_{cf}, T)$ which in a trivial fashion partly (or even wholly) satisfy the hypothesis proposed.

With the programme for testing the proposed hypothesis outlined, we are going to apply it to N_2, Xe and propylene fluids. Thereby, the problem immediately arises as how to get experimental isothermal P, ϱ data accurate enough to avoid fitting experimental errors and deciding which value of ϱ_{cf} enables us to fit them best. This problem is especially troublesome in view of the fact that we are able to fit, e. g. collated P, ϱ data of 150°C isotherm of N_2 over the whole available density range $\varrho \in [0, 3.6\,\varrho_c]$ by ansatzes $P^*(\varrho, m-2, n-2, T)$ with an average accuracy of about 2% and 0.2% for $m-2 = n-2 = 4$ and $m-2 = n-2 = 5$, respectively; whereby the accuracy of these data optimistically estimated is not much greater than, say 0.1 %.

Jacobsen and Stewart$^{5)}$ have obtained an analytic equation of state for N_2 gas, say $P_{JS}(\varrho, T)$, which with an accuracy of about 1% represents a large number of experimental P, ϱ, T data over a wide range of temperatures and densities - up to ten times the critical temperature and 3.6 times the critical density. So it is reasonable to assume that:

i) for those isotherms where experimental P, ϱ data are available for densities up to 3.6 ϱ_c the empirical equation of state $P_{JS}(\varrho, T)$ yields an approximation to the »true« isothermal pressure-density dependence of N_2 better than we can obtain by fitting directly experimental P, ϱ data of a single isotherm, and

ii) for those isotherms where experimental P, ϱ data are not known for densities up to 3.6 ϱ_c the analytic expression $P_{JS}(\varrho, T)$ gives usable values of pressure-density dependence up to the fluid densities of 3.6 ϱ_c. Therefore, in what follows we will assume that the analytic expression $P_{JS}(\varrho, T)$ represents the actual P, ϱ, T surface of N_2 fluid in the region $\varrho \in [0, 3.6\ \varrho_c]$ and $T \in [0, 14\ T_s]$ with an accuracy between 0.1 % and 1 %. using the nitrogen equation of state $P_{JS}(\varrho, T)$[5] we generated thirty six synthetic pressure values P_i corresponding to densities $\varrho_i = i\ 3.6\ \varrho_c/36$, $i = 1, 2, \ldots, 36$, for isotherms $T = 150°\mathrm{C} = 3{,}35\ T_c$ and $T = 800°\mathrm{C} = 8.50\ T_c$. On calculating ratios $R(m, n, \varrho_{cf}, T)$ as defined by (12) for $m = n = 6$, $m = n + 1 = 7$, $m + 1 = n = 7$, and $m = n = 7$ as functions of $\varrho_{cf}/\varrho_c \in [2.8, 5.8]$, we plotted the results obtained in Figs. 1 and 2. We see that in the case of $\mathrm{N_2}$ fluid for any value of $\varrho_{cf} \geq 3.9\ \varrho_c$ all the results in Figs. 1 and 2 support the hypothesis proposed.

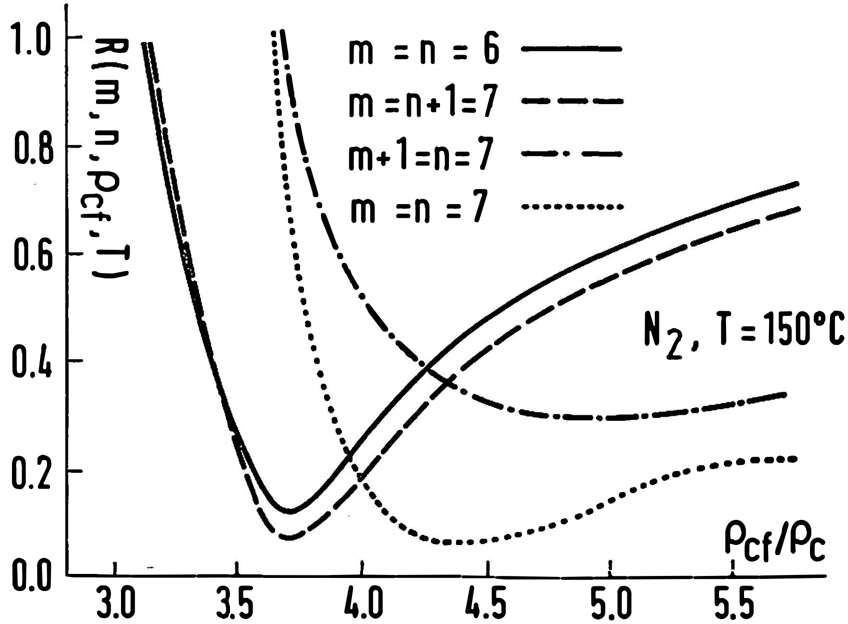

Fig. 1: Values of the ratios $R(m, n, \varrho_{cf}, T = 150°\mathrm{C})$, $m = n = 6$, $m = n + 1 = 7$, $m + 1 = n = 7$, $m = n = 7$, indicating how much the fitability of rational ansatzes is increased by assuming relation (6) at $\varrho = \varrho_{cf}$, are plotted versus the reduced values of ϱ_{cf} for 150°C isotherm of $\mathrm{N_2}$ fluid.

Juza and Šifner[6] developed an equation of state for Xe which reproduces experimental P, ϱ, T data with an accuracy of about 0.1 % for temperatures up to $3T_c$ and densities up to 3 ϱ_c. Using this equation of state for Xe fluid, we generated thirty six synthetic pressure values P_i corresponding to densities $\varrho_i = \mathrm{i}\ 3\ \varrho_c/36$, $\mathrm{i} = 1, 2, \ldots, 36$, for for $306°\mathrm{C} = 2T_c$ and $1176°\mathrm{C} = 5T_c$ isotherms and calculated the corresponding ratios as functions of $\varrho_{cf} \in [2.8\varrho_c, 5.8\varrho_c]$. For these values of ϱ_{cf} the ratios $R(m = 6, n = 6, T = 2T_c$ or $5T_c)$, $R(m = 7, n = 6, T = 2T_c$ or $5T_c)$ and $R(m = 6, n = 7, T = 2T_c)$ assume values greater than one

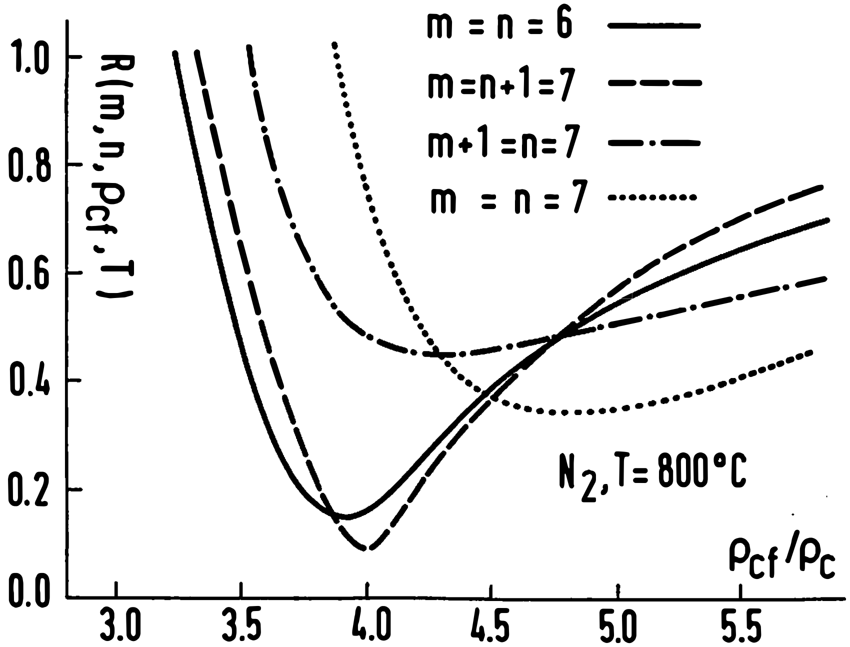

Fig. 2: For N_2 fluid values of $R\,(6, 6, \varrho_{cf}, 800°\mathrm{C})$, $R\,(6, 7, \varrho_{cf}, 800°\mathrm{C})$, $R\,(7, 6, \varrho_{cf}, 800°\mathrm{C})$ and $R\,(7, 7, \varrho_{cf}, 800°\mathrm{C}$ plotted versus ϱ_c/ϱ_c.

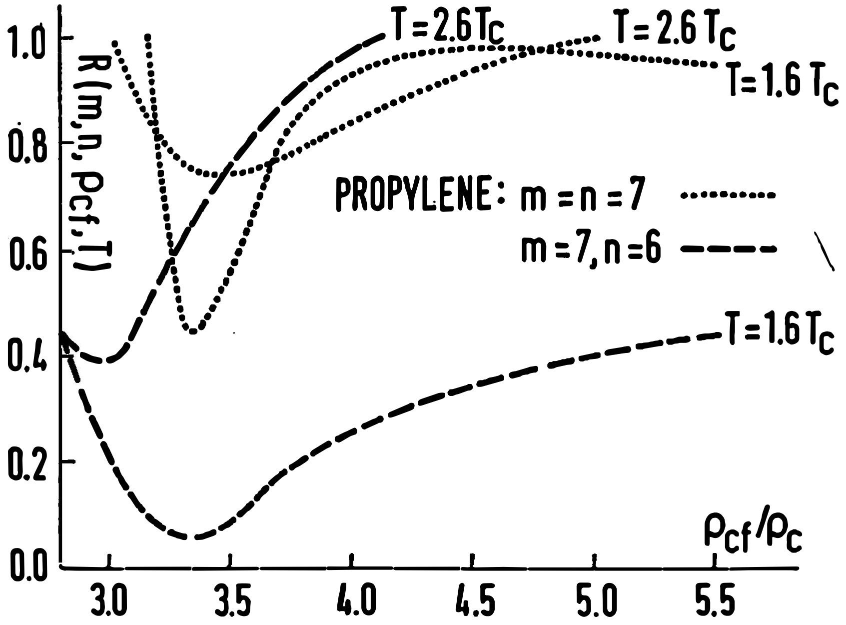

Fig. 3: For propylene fluid values of $R\,(m, n, \varrho_{cf}, T = 1.6\ T_c$ and $2.6\ T_c)$ are plotted versus reduced values of ϱ_{cf} for $m = n = 7$ and $m = 7, n = 6$ using dotted and dashed lines, respectively.

and do not support the hypothesis considered, whereas ratios $R\,(m = 6, n = 7, T = 5T_c)$ and $R\,(m = 7, T = 2T_c$ or $5T_c)$ do so for $\varrho_{cf} \geq 3\,\varrho_c$. Hence these results present less evidence in support of the hypothesis considered than those obtained for N_2 fluid. This may be due to the fact that now all the ansatzes $P^*\,(\varrho, m-2, n-2, T)$ used for comparison in calculating ratios (12) were able to fit synthetic isothermal P, ϱ data of Xe with an accuracy greater than 0.15%.

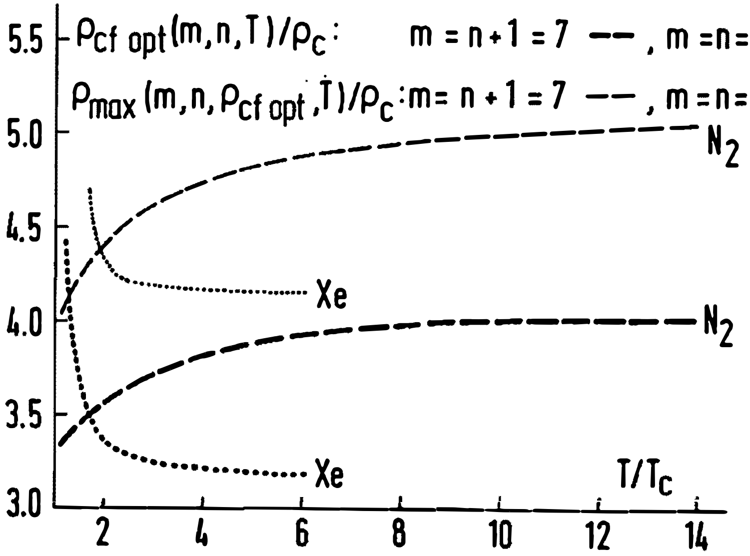

Fig. 4: The thick dashed and dotted lines plot the temperature dependence of the reduced optimal values of $\varrho_{cf\ opt}\,(m = 7, n = 6, T, N_2)$ and $\varrho_{cf\ opt}\,(m = 7, n = 7, T, Xe)$, respectively, which optimize the fit of isothermal P, ϱ dependences of N_2 and Xe over density intervals $\varrho \in [0, 3.6\varrho_c]$ and $\varrho \in [0, 3\varrho_c]$ by rational functions $P\,(\varrho, 7, 6, \varrho_{cf}, T)$ and $P\,(\varrho, 7, 7, \varrho_{cf}, T)$, respectively. Using thin dashed and dotted lines are plotted the temperature dependences of the corresponding reduced maximal densities $\varrho_{max}\,(7, 6, \varrho_{cf\ opt}, T)$ of N_2 and $\varrho_{max}\,(7, 7, \varrho_{cf\ opt}, T)$ of Xe, respectively.

De Reuck and Armstrong[7] produced an equation of state for propylene reproducing experimental P, ϱ, T data with an accuracy between 0.1% and 2% for temperatures up to $1.6\,T_c$ and densities up to $2.9\,\varrho_c$. Using this propylene equation of state we generated synthetic experimental P_i values corresponding to $\varrho_i = i\,2.9\,\varrho_c/36$, $i = 1, 2, \ldots, 36$ for $1.6\,T_c$ and $2.6\,T_c$ isotherms, and calculated corresponding ratios as functions of $\varrho_{cf} \in [2.8\,\varrho_c, 5.8\,\varrho_c]$. For these values of ϱ_{cf} the ratios $R\,(m = 6, n = 6, T = 1.6\,T_c$ or $2.6\,T_c)$ and $R\,(m = 6, n = 7, T = 1.6\,T_c$ or $2.6\,T_c)$ are greater than one; whereas the ratios $R\,(m = 7, n = 6, T = 1.6\,T_c$ or $2.6\,T_c)$ and $R\,(m = 7, n = 7, 1.6\,T_c$ or $2.6\,T_c)$ all support the hypothesis proposed for values of $\varrho_{cf} \in [3.2\,\varrho_c, 4.1\,\varrho_c]$, Fig. 3. Comparative ansatzes $P^*\,(m-2, n-2, T = 1.6\,T_c)$, $m = n = 6$, $m = n + 1 = 7$, $m + 1 = n = 7$ and $m = n = 7$, fit P_i, ϱ_i data with an average accuracy of 1.4%, 1.3%, 0.5% and 0.06 %, respectively.

Gathering from Figs. 1 and 2 that for N_2 fluid the optimal values of ϱ_{cf} which minimize the ratios $R\,(m, n, \varrho_{cf}, T)$, say $\varrho_{cf\ opt}\,(m, n, T)$ do not seem to depend very much on temperature, we calculated $\varrho_{cf\ opt}\,(m = 7, n = 6, T)$ for N_2 fluid as a function of $T/T_c \in [1,14]$ and $\varrho_{cf\ opt}$ $(m = 7, n = 7, T)$ for Xe fluid as a function of $T/T_c \in [1,6]$. The results obtained are plotted on Fig. 4, and they show that the optimal values of ϱ_{cf} depend very little on temperature T indeed. This fact may be interpreted as supporting the hypothesis proposed; it agrees also with expectations based on Thom's theory of catastrophes according to which the optimal ϱ_{cf} should be temperature independent if it is associated with a liquid-solid phase transition, for a detailed analysis of this point cf. Ribarič and Žekš4). The preceding results3,4); though suggesting relation (6) at $\varrho = \varrho_{cf} \in [3\varrho_c, 7\varrho_c]$, gave no indications that the value of ϱ_{cf} might be temperature independent.

3. *Maximal isothermal density*

Preceding studies8) of the isothermal P, ϱ dependence of real fluids have shown for the highest measured fluid densities the isothermal pressure increases as some power of ϱ, say $P \approx \varrho^n$ with $n = 4 - 5$. These results are contrary to those expected from computer simulation studies of a hard sphere gas which suggest that its isothermal pressure exhibits a pole-like behaviour, say $P \approx (\varrho_{max} - \varrho)^{-1}$, 9,10), because they8) show that in the region of the highest measured densities the isothermal P, ϱ dependence of a real fluid definitely gives no indications of pole-like behaviour.

Having spherical molecules with diameter σ, there are two ways of arranging them so as to obtain maximal density: the hexagonal close-packed structure and the face centered cubic structure. They both result in a minimal molar volume, say $V_{min} = N_o \sigma^3/\sqrt{2}$, N_o being Avogadro's number. The pressure of non-interacting rigid spheres with diameter σ tends to infinity11) as its molar volume V tends isothermally towards its minimal value $V_{min} = N_o \sigma^3/\sqrt{2}$. Diameter σ being equal to the minimal distance between centres of rigid shperes, we way expect that for a real gas the extrapolated values of its isothermal pressure will tend to infinity as its molar volume tends toward some effective minimal molar volume, say $V_{min\ ef} = N_o (\bar{d}_{min})^3/\sqrt{2}$, where $\bar{d}_{min}$ is a kind of effective hard core diameter equalling some average (possibly temperature dependent) minimal distance between any two molecular centres. Let us estimate d_{min} and $V_{min\ ef}/V_c$ using square-well, Lennard-Jones and Kihara intermolecular potential functions whose potential parameters have been determined by fitting experimentally determined values of the second virial coefficient, cf. Sherwood and Prausnitz12). In the case of the square-well potential, the minimal distance between molecular centres d_{min} equals the diameter σ of its hard-core and does not depend on the kinetic energy of colliding molecules. Fitting virial coefficients $B(T)$ of argon between 0.55 T_c and 5.78 T_c, they obtained $\sigma = 30.67$ nm resulting in $V_c/V_{min\ ef} = 6.13$; and fitting experimental $B(T)$ data for nitrogen N_2 between T_c and 5.34 T_c they obtained $\sigma = 32.77$ nm resulting in $V_c/V_{min\ ef} = 5.95$. In the case of the Lennard-Jones potential, the minimal distance between two colliding molecules depends on their collision energy, equalling on average $\frac{1}{2} kT$ and so depends on temperature T. Using the Lennard-Jones potential parameters of Sherwood and Prausnitz12), and those collected in Hansen and McDonald13), we infer that for zero colliding energy the calculated minimal distance d_{min} of Ne, Ar, Kr, Xe, CH_4 and N_2 results in $V_c/V_{min\,ef} = 4.71$, 4.48, 4.34, 4.18, 4.18 and 4.00, respectively; whereas for a colliding energy of $\frac{1}{2} k\, 10\, T_c$ we get $V_c/V_{min\,ef} = 6.39$, 6.09, 5.90, 5.69, 5.69 and 5.47, respectively. Analogously taking the Kihara potential parameters of Sherwood and Prausnitz[12], we get for Ar and N_2 the estimates $V_c/V_{min\,ef} = 4.85$ and 4.78, respectively, at zero colliding energy, and $V_c/V_{min\,ef} = 6.24$ and 5.94 for a colliding energy of $\frac{1}{2} k\, 10\, T_c$.

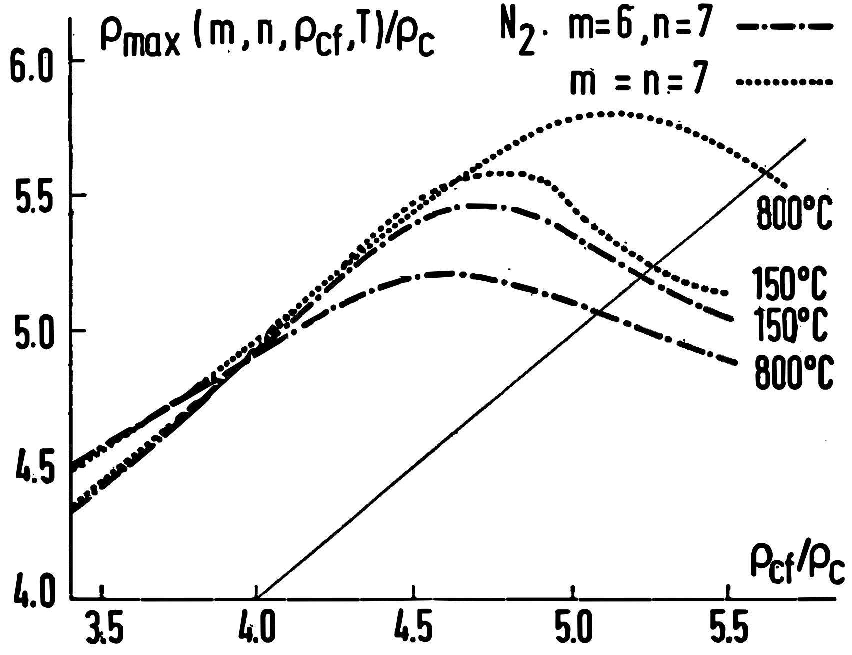

Fig. 5: Reduced values of maximal densities ϱ_{max} ($m = 7$, $n = 7$, ϱ_{cf}, T) and ϱ_{max} ($m = 6$, $n = 7$, ϱ_{cf}, T) are plotted versus $\varrho_{cf}/\varrho_c \in [3.4, 5.8]$ for 150°C and 800°C isotherms of N_2 fluid. Using the thin line we plotted $\varrho_{max} = \varrho_{cf}$.

These considerations suggest checking the rational representations $P(\varrho, m, n, \varrho_{cf}, T)$ of isothermal pressure-density dependences of N_2, Xe and propylene fluids to see whether they exhibit a pole at some density, say $\varrho_{max} = \varrho_{max}(m, n, \varrho_{cf}, T)$ within the density intervals $[3.6\, \varrho_c, 6\varrho_c]$ and $[3\, \varrho_c, 6\varrho_c]$, respectively. And indeed they do so. For isotherms $T = 150$°C and $T = 800$°C of N_2 fluid we plotted ϱ_{max} $(m, n\, \varrho_{cf}, T)$ as a function of $\varrho_{cf}/\varrho_c \in [3.4, 5.8]$ for $m = n = 7$, and $m + 1 = n = 7$ in Fig. 5. We see that the values of ϱ_{max} do not depend much on the values of ϱ_{cf}, m and n; they agree with the preceding estimates of the maximal density we derived from intermolecular potential functions. Rational representations $P(\varrho, m = 6, \varrho_{cf}, T = 150°C$ or $800°C)$ and $P(\varrho, m = 7, n = 6, \varrho_{cf}, T = 150°C$ or $800°C)$ of isothermal P, ϱ dependence of N_2 fluid exhibit two poles which disappear by coalescing for smaller and larger values of ϱ_{cf}, cf. Fig. 6. In the case of Xe fluid, poles of $P(\varrho, m = 6, n = 7, \varrho_{cf}, T = 2T_c)$ and $P(\varrho, m = 7, n = 7, \varrho_{cf}, T = 2T_c$ or $5T_c)$ exhibiting similar behaviour are plotted versus ϱ_{cf} in Fig. 7; again we see that values of maximal density for Xe fluid agree with preceding estimates. In Fig. 8 we plotted poles $\varrho_{max}(m, n, \varrho_{cf}, T)$ of $P(\varrho, 7, 6, \varrho_{cf}, T)$ and $P(\varrho, 7, 7, \varrho_{cf}, T)$ for $1.6T_c$ and $2.6T_c$ isotherms of propylene as functions of $\varrho_c \in [3\varrho_c, 5.5\ \varrho_c]$.

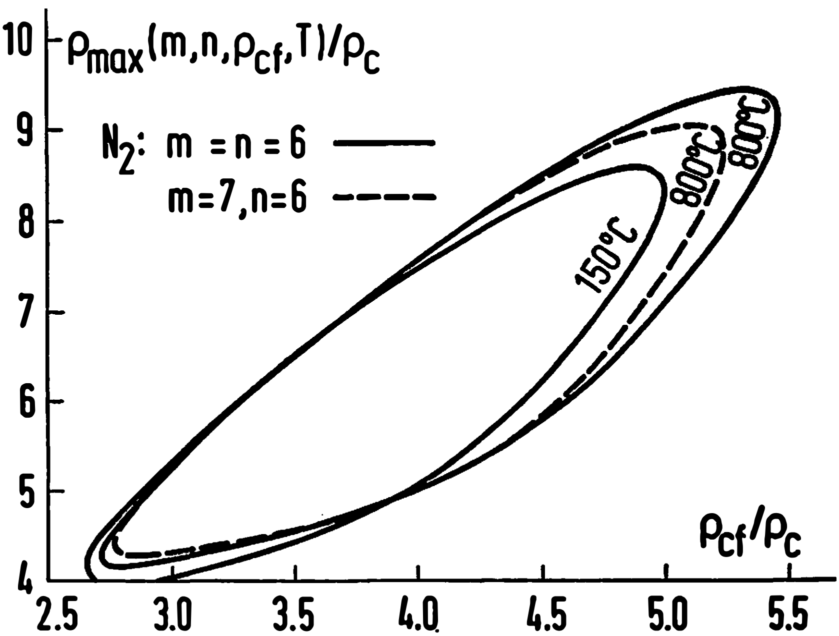

Fig. 6: Reduced values of maximal densities $\varrho_{max}(m = 6, n = 6, \varrho_{cf}, T)$ and $\varrho_{max}(m = 7, n = 6, \varrho_{cf}, T)$ are plotted for 150°C and 800°C isotherms of N_2 fluid, plots for 150°C isotherms being too close to be distinguished.

Consequently the results obtained indicate that (i) the pole *of* $P(\varrho, m, n, \varrho_{cf}, T)$ at $\varrho = \varrho_{max}$ is an inherent property of the isothermal P, ϱ dependences of the real fluids considered, and (ii) the information about the molecular size is directly contained in isothermal P, ϱ data of the real fluids considered: Baram and Luban[11] have shown an analogous fact that the first six terms of a virial series for hard discs and hard spheres contain information about the density of closest packing.

In Fig. 4 we also plotted the temperature dependence of the zeros $\varrho_{max}(7,6, \varrho_{cf\,opt}(7,6,T), T)$, and $\varrho_{max}(7, 7, \varrho_{cf\,opt}(7,7,T), T)$ of denominators of optimal fits $P(\varrho, 7, 6, \varrho_{cf\,opt}(7, 6, T)\ T)$ and $P(\varrho, 7, 7, \varrho_{cf\,opt}(7, 7, T), T)$ of isotherms of N_2 and Xe fluids, respectively.

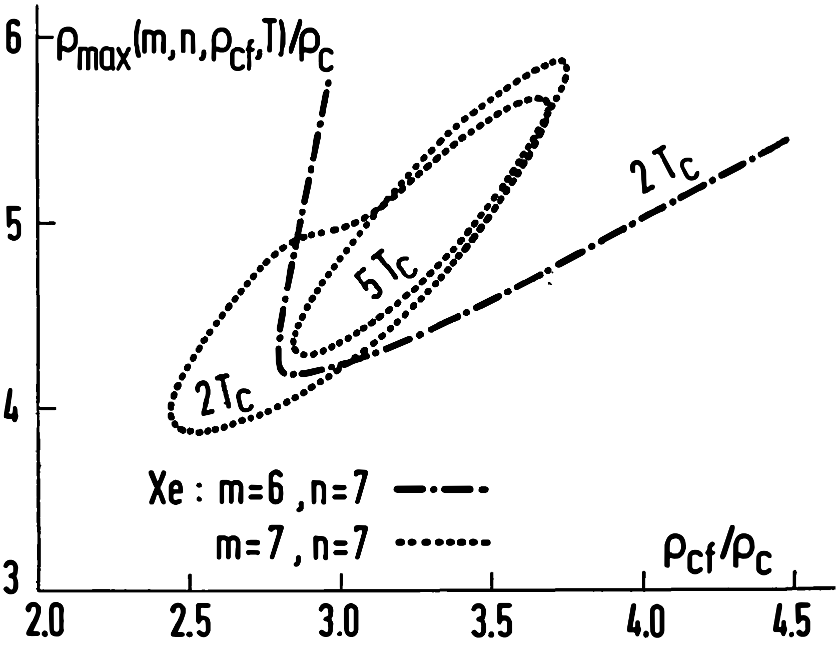

Fig. 7: Reduced values of singularities of rational representations $P(\varrho, m, n, \varrho_{cf}, T)$ of isothermal P, ϱ dependence of Xe fluid are plotted versus ϱ_{cf}/ϱ_c.

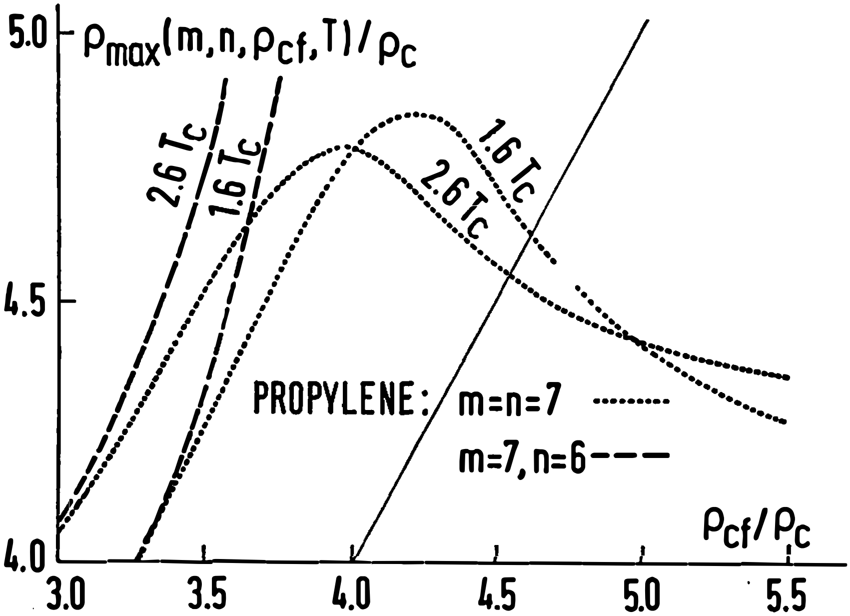

Fig. 8: Reduced values of maximal densities ϱ_{max} ($m = 7$, $n = 6$, ϱ_{cf}, T) and ϱ_{max} ($m = 7$, $n = 7$, ϱ_{cf}, T) are plotted using dashed and dotted lines, respectively, for 1.6 T_c and 2.6 T_c isotherms of propylene. Using the thin line we plotted $\varrho_{max} = \varrho_{cf}$.

4. *Discussion*

On investigating the analytic properties of isothermal pressure density relations of real fluids we proposed the hypothesis that outside the critical region ($T \approx T_c$ and $\varrho \approx \varrho_c$) the isothermal equation of state of real gases is a rational function $P(\varrho, m, n, \varrho_{cf}, T)$ as defined by (5, 6, 9) with m and n possibly being infinite and ϱ_{cf} being temperature independent. The experimental evidence in support of this hypothesis is as follows:

1) Preceding investigations[1,2] brought forth that for non-critical isotherms the P, ϱ dependence of a real gas can be well represented locally in the vicinity of the critical density by a rational ansatz satisfying condition (6) at $\varrho = \varrho_{cc} \approx \varrho_c$. The results of this paper give an indication that the additional assumption of condition (6) at $\varrho = \varrho_{cf}$, with ϱ_{cf} being temperature independent, does make some rational functions more effective for fitting isothermal P, ϱ data of the real fluids considered. This fact implies that property (6) at $\varrho = \varrho_{cf}$ is an inherent property of isothermal P, ϱ data of the real fluids considered, despite the fact that the estimated value of ϱ_{cf} lies in the region of the solid state densities.

2) On being fitted to isothermal P, ϱ data of the real fluids considered, the rational ansatz $P(\varrho, m, n, \varrho_{cf}, T)$ automatically implies the existence of a maximal density ϱ_{max} beyond which a real fluid cannot be compressed, i. e. beyond which P, ϱ dependence will be markedly different. The notion of closest packing relates directly the maximal density to the effective diameters of the molecules involved. Thus by fitting isothermal P, ϱ data by ansatzes $P(\varrho, m, n, \varrho_{cf}, T)$ we can obtain estimates of the size of the corresponding molecules in a conceptually most simple and direct way. We have shown that these estimates agree qualitatively with estimates of molecular size obtained via calculations based on certain assumptions of statistical physics.

In the preceding paper[4] we discussed the possibility that the existence of property (6) at $\varrho = \varrho_{cf}$ might indicate that isothermally compressed real fluids in the region of solid state densities anticipate a certain kind of phase transition from liquid to some amorphous glass-like state. We note, however, that all rational representations $P(\varrho, m, n, \varrho_{cf}, T)$ considered extrapolate isothermal pressure as a monotonically increasing function of ϱ which tends to infinity as ϱ increases towards ϱ_{max}. This monotonous behaviour of the extrapolated pressure neither supports nor contradicts the possibility discussed. It may be due of course to the fact that the considered rational ansatzes $P(\varrho, m, n\, \varrho_{cf}, T)$ do not have enough terms to display wiggles which would strongly suggest that condition (6) at $\varrho = \varrho_{cf}$ is indeed related to a certain kind of anticipated phase transition.

Preceding results[4] obtained by analyzing the extrapolated behaviour of some empirical equation of state suggested that the values of $\varrho_{cf} \in [3\varrho_c, 7\varrho_c]$. The results of this present paper enable us to infer more directly from experimental data three additional compatible estimates about the »true« value of the parameter ϱ_{cf}:

i) The most direct estimate of the »true« value of ϱ_{cf} is provided by looking for those values ϱ_{cf} which make some ratios $R(m, n, \varrho_{cf}, T) < 1$.

This way we obtain for N_2, Xe and propylene fluids estimates $\varrho_{cf} \geq 3.9\, \varrho_c$, $\varrho_{cf} \geq 3\, \varrho_c$ and $\varrho_{cf} \in [3.2\, \varrho_c, 4.1\, \varrho_c]$, respectively, cf. Figs. 1, 2, 3.

ii) If ϱ_{cf} is indeed related to a certain kind of liquid-solid phase transition and $\varrho_{max}(T)$ to a maximal possible isothermal density, then their values are expected to satisfy relation

$$\varrho_{cf} < \varrho_{max}(T) \ \forall \ T. \tag{13}$$

On assuming that $\varrho_{max}(m, n, \varrho_{cf}, T)$ have to satisfy an analogous relation, Figs. 5 and 8 suggest upper bounds $\varrho_{cf} \leq 5.1\ \varrho_c$ and $\varrho_{cf} \leq 4.5\ \varrho_c$ for N_2 and propylene fluids.

iii) The pole of a rational representation $P(\varrho, m, n, \varrho_{cf}, T)$ of isothermal P, ϱ dependence having a physical meaning, we can conclude from its disappearance for too large or too small values of ϱ_{cf} in Figs. 6 and 7 the estimates $\varrho_{cf} \in [2.7\ \varrho_c, 5.4\ \varrho_c]$ and $\varrho_{cf} \in [2.5\ \varrho_c, 3.7\ \varrho_c]$ for N_2 and Xe liquids, respectively.

Summing up all these estimates we can reasonably expect for all three fluids considered that their »true« value of $\varrho_{cf} \in [3\ \varrho_c, 5\varrho_c]$.

The results obtained in this paper are inferred by comparing fits whose accuracy is not substantially smaller than the estimated accuracy of the underlying experimental data. We may derive from them, therefore, only qualitative information about the properties of the »true« isothermal equations of state of real fluids considered. So the results of this paper indicate the existence of two new kinds of material constants characteristic of real fluids and associated with rational representations $P(\varrho, m, n, \varrho_{cf}, T)$ of their isothermal P, ϱ dependences:

i) a temperature independent constant ϱ_{cf} which as yet has not been even conceptually known; and

ii) a maximal density ϱ_{max} possibly temperature dependent and conceptually directly related to the effective hard-core diameter.

The given physical interpretations of the results obtained concerning the rational representations $P(\varrho, m, n, \varrho_{cf}, T)$ of isothermal P, ϱ dependences of real fluids — ϱ_{cf} temperature independent, pole at ϱ_{max} — do not imply any notion of extrapolation in the sense that they predict what would happen were we to compress a real fluid beyond the largest experimentally measured density used in determining empirical equations of state analysed. Rather they are properties of measured experimental P, ϱ, T data of the real fluids considered, though manifesting themselves explicitly in the properties of $P(\varrho, m, n, \varrho_{cf}, T)$ in the region of solid state densities.

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ZNAČILNOSTI P, ϱ, T PLOSKEV REALNIH TEKOČIN V OBMOČJU GOSTOT TRDNEGA STANJA

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Originalno znanstveno delo

Na primeru N_2, Xe in propilena smo pokazali koristnost zapisa nadkritične izotermne odvisnosti pritiska od gostote z racionalnimi funkcijami oblike $P(\varrho) = A(\varrho, m)/B(\varrho, n)$, kjer sta A in B taka polinoma m in n stopnje, da je

$$\partial^2 A/\partial\varrho^2 = \partial^4 A/\partial\varrho^4 = \partial^2 B/\partial\varrho^2 = \partial^4 B/\partial\varrho^4 = 0$$

pri kritični gostoti ϱ_c in pri neki temperaturno neodvisni gostoti $\varrho_{cf} \in [3\varrho_c, 5\varrho_c]$. Take predstavitve izotermne odvisnosti pritiska od gostote imajo pole prve stopnje pri gostoti $\varrho_{max} \in [4\varrho_c, 6\varrho_c]$, kateri odgovarjajo velikosti dušikovih in ksenonovih molekul, ki so v soglasju z ocenami dobljenimi iz efektivnih potencialov.