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LOCAL ANTISYMMETRIES OF ISOTHERMAL BEHAVIOUR OF THE LENNARD-JONES AND REAL FLUIDS

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Analyzing the above-critical isothermal behaviour of a variety of experimentally determined equations of state of the Lennard — Jones, N_2, Xe, Ar, ethane, propane, n-pentane, ethylene and propylene fluids, we found evidence suggesting $\partial^4 P/\partial \varrho^4$ is strongly antisymmetric in the vicinity of $(1 \pm 0.1)\, \varrho_c$ and $(2.7 \pm 0.3)\, \varrho_c$, ϱ_c being the critical density, and that the second isothermal derivative of the chemical potential is antisymmetric in the vicinity of $(2.7 \pm 0.3)\, \varrho_c$.

1. *Introduction*

First local antisymmetry of the isothermal behaviour of real gases was discovered by Tisza and Chase[1] about fifteen years ago, when they concluded that the antisymmetry of the chemical potential

$$\mu(\varrho, T) \equiv \mu(\varrho_c, T) + \int_{\varrho_c}^{\varrho} \varrho^{-1} \frac{\partial P}{\partial \varrho} \mathrm{d}\varrho \tag{1}$$

as a function of $(\varrho - \varrho_c) \approx 0$, ϱ_c being the critical density, may be a fundamental property of real fluids, at least in the vicinity of the critical temperature. Vicentini — Missoni, Levelt Sengers and Green[2] subsequently showed graphically that the chemical potential μ of CO_2, Ar and ^{4}He as a function of $(\varrho - \varrho_c)$ indeed looks antisymmetric over a range of densities up to nearly 50% from the critical density ϱ_c, and up to temperatures far above critical. Ribarič and Žekš[3] pointed out that the observed local antisymmetry of the chemical potential μ along the density line, say $\varrho = \varrho_{cc} \approx \varrho_c$ implies that for any isotherm $T > T_c$ we have

$$\partial^2\mu/\partial\varrho^2 = 0 \tag{2}$$

at $\varrho \approx \varrho_c$. They found assumption (2) at $\varrho = \varrho_c$ for all $T > T_c$ compatible with experimental data for Xe, CO_2, N_2, ethylene and propene, if the experimental $P/RT\varrho$ values considered are changed, on average, by about 0.05%.

Two years ago Ribarič and Žekš[4] found that the real fluids considered display locally an additional isothermal antisymmetry in the high density region in the vicinity of the density $(2.7 \pm 0.3)\,\varrho_c$. They showed that the logarithm of the compressibility $z = P/TR\varrho$ of the real fluid considered is strongly antisymmetric along the density line, say $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\,\varrho_c$. By being mainly exhibited locally for densities where experimetal data are scarce, this marked antisymmetric behaviour of $\ln z$ is mainly an extrapolated property of the available experimental data. For N_4, however, the necessary high density experimental data were available and they found them compatible with a related assumption that

$$\partial^2 \ln z/\partial\varrho^2 = 0 \ \forall\ T \gtrsim T_c \tag{3}$$

at $\varrho = 2.7\,\varrho_c$.

So there is strong experimental evidence suggesting that P, ϱ, T surfaces of real fluids have two lines of symmetries: the first one exhibiting itself in the local antisymmetry of the associated chemical potential μ along the density line, say $\varrho = \varrho_{cc} = (1 \pm 0.1)\,\varrho_c$ and the second one exhibiting itself in the antisymmetry of the logarithm of the compressibility factor $P/RT\varrho$ along the density line, say $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\,\varrho_c$.

Recently, Nicolas, Gubbins, Streett and Tildesley[5] have collated comprehensive computer simulation data about the Lennard-Jones fluid and represented them by *a* Jacobsen-Stewart's (i. e. modified Benedict-Webb-Rubin) equation having 32 constants. This equation, say $P_I(\varrho, T)$ reproduces computed P, ϱ, T data well over the density range $\varrho \in [0, 3.4\,\varrho_c]$ and the temperature range $T \in [0.37\,T_c, 4.4\,T_c]$; empirical equations of state approximating P, ϱ, T surfaces over so an extensive range are few. Using this equation $P_I(\varrho, T)$ we will try to infer the properties of the P, ϱ, T surface of the Lennard-Jones fluid in the vicinity of the density lines $\varrho = \varrho_{cc} = (1 \pm 0.1)\,\varrho_c$ and $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\,\varrho_c$. In particular we will check whether:

a) the chemical potential μ and the compressibility factor z of the Lennard-Jones fluid exhibit the same kind of antisymmetries observed in real fluids;

b) $\ln z$ or any of its higher derivatives exhibit certain symmetry in the vicinity of the density line $\varrho = \varrho_{cc}$;

c) the chemical potential μ ot any of its higher derivatives exhibit some symmetry in the vicinity of the density line $\varrho = \varrho_{ac}$;
d) the pressure P or any of its higher derivatives $\partial^i P / \partial \varrho^i$, $i = 1, 2, \ldots, 20$, exhibit any kind of symmetry in the vicinity of the density lines $\varrho = \varrho_{cc}$ or $\varrho = \varrho_{ac}$.

In the next section we are going to investigate the first three questions and compare the results obtained for the Lennard—Jones fluid with the corresponding properties of N_2, argon, propane and ethane fluids. In the subsequent section we will consider the fourth question for the Lennard-Jones, argon, xenon, propane, ethane ethylene and n-pentane fluids.

2. *Symmetries and antisymmetries of the chemical potential μ, of the compressibility z, and of their derivatives*

a) *Methodology and data*

Possible local isothermal antisymmetry (symmetry) of, say $\partial^{i_0} \mu / \partial \varrho^{i_0}$, $i_0 = 0, 1, \ldots$, along some density line, say $\varrho = \varrho_0$ will manifest itself in the fact that $\partial^{i_0 + 2j} \mu / \partial \varrho^{i_0 + 2j}$,

$$j = 1, 2, \ldots, j_{max}, \; [\partial^{i_0 + 2j + 1} \mu / \partial \varrho^{i_0 + 2j + 1}, j = 0, 1, \ldots, j_{max}]$$

will have zeros, say $\varrho_\mu^{(i_0 + 2j)}(T) = \varrho_0 \; [\varrho_\mu^{(i_0 + 2j + 1)}(T) = \varrho_0] \; \forall \; T$. Hence the search for possible local isothermal antisymmetries and symmetries of the chemical potential μ and of its derivatives $\partial^i \mu / \partial \varrho^i$ can be conducted simply by computing values of its partial derivatives $\partial^i \mu / \partial \varrho^i$ and checking whether in the vicinity of the density lines $\varrho = \varrho_{cc} = (1 \pm 0.1)\, \varrho_c$ and $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\, \varrho_c$ there are zeros $\varrho_\mu^{(i)}(T)$ which are temperature independent. And the same goes for possible antisymmetries and symmetries of $\partial^i \ln z / \partial \varrho^i$.

So far so good. However, when trying to find out what kind of temperature independent isothermal symmetries the chemical potential $\mu(\varrho, T)$ and the logarithm of the compressibility factor $\ln(P/RT\varrho)$ of the fluid considered display in the vicinity of the density lines $\varrho = \varrho_{cc}$ and $\varrho = \varrho_{ac}$, we have to take into account that for no real or model fluid considered do we know the required exact equation of state, say $P = P(\varrho, T)$. For some fluids there is an approximation to $P(\varrho, T)$ supplied by an empirical equation of state, say $P_{exp}(\varrho, T)$ which reproduces certain available experimental data. Almost a century's experience in fitting experimental P, ϱ, T data by various analytic ansatzes indicates that outside the critical region $\varrho \approx \varrho_c$ and $T \approx T_c$ they can be sufficiently well represented by empirical equations of state of the following form

$$P_{exp}(\varrho, T) = RT\varrho + \sum a_{ij} \varrho^i T^{-j/2} + w(\varrho) \sum b_{kl} \varrho^{2k+1} T^{-l}, \qquad (4)$$

where $w(\varrho)$ usually equals $\exp - (\varrho/\varrho_c)^2$ or zero. The true isothermal pressure density dependence $P(\varrho, T)$ being unavailable for investigating whether some isothermal derivative of $\partial \mu / \partial \varrho = \varrho^{-1} \partial P / \partial \varrho$ or of $\ln(P/RT\varrho)$ has temperature independent zeros within the density intervals $[0.9\, \varrho_c, 1.1\, \varrho_c]$ and $(2.4\, \varrho_c, 3\, \varrho_c]$, we will have to make do with any available approximate empirical equation of state $P_{exp}(\varrho, T)$ by analyzing zeros, say $\varrho_{\mu\, exp}^{(l)}(T)$ and $\varrho_{\ln\, z\, exp}^{(l)}(T)$ of isothermal derivatives $\partial^l \mu_{exp}/\partial \varrho^l = \partial^{l-1} (\varrho^{-1}\, \partial P_{exp}/\partial \varrho)/\partial \varrho^{l-1}$ and $\partial^l \ln (P_{exp}/RT\varrho)/\partial \varrho^l$, respectively. Thereby we will be looking for those of the zeros $\varrho_{\mu\, exp}^{(l)}(T)$ and $\varrho_{\ln\, z\, exp}^{(l)}(T)$ which for all relevant isotherms stay in the vicinity of ϱ_c or 2.7 ϱ_c, hoping thereby that their existence implies that the corresponding exact zeros $\varrho_{\mu}^{(l)}(T)$ and $\mu_{\ln\, z}^{(l)}(T)$ are truly temperature independent and close to $\varrho = \varrho_c$ or to $\varrho = 2.7\, \varrho_c$. There is, of course, a very distinct possibility that the isothermal behaviour of a derivative, say $\partial^l \mu_{exp}/\partial \varrho^l$ substantially differs from the isothermal behaviour of the corresponding exact derivative $\partial^l \mu/\partial \varrho^l$ of the fluid considered. And so it is quite possible that an approximate local isothermal antisymmetry displayed by $\partial^{l-2} \mu_{exp}/\partial \varrho^{l-2}$ is not an indication of the existence of the temperature independent local antisymmetry in $\partial^{l-2} \mu/\partial \varrho^{l-2}$, but is rather due to the particular ansatz $P_{exp}(\varrho, T)$ used to represent the experimental data. It would of course be possible for us to detect such a misleading possibility had we at our disposal a few additional different empirical equations of state (4) approximating the true but unavaliable equation of state $P(\varrho, T)$. Then it would be reasonable to assume that an antisymmetry displayed by different approximate equations of state of the same fluid is also common to the true $P(\varrho, T)$ and thus an intrinsic physical property of the fluid considered.

Unfortunately, researches providing an empirical equation of state for a given gas do usually give only one analytic form reproducing the collected experimental P, ϱ, T data, e. g. $P_{\mathrm{I}}(\varrho, T)$ for the Lennard-Jones fluid[5]. To obtain additional analytic approximations, say $P_k(\varrho, T)$, $k = 2, 3, \ldots$, to the true, yet unknown equation of state $P(\varrho, T)$ of the Lennard-Jones fluid, we proceed as follows. First we take a short cut by generating a set of N synthetic experimental P, ϱ, T data by evaluating the pressure, say $P_l = P_{\mathrm{I}}(\varrho_l, T_l)$ at N different T_l, ϱ_l points belonging to the region of validity of the empirical equation of state $P_{\mathrm{I}}(\varrho, T)$; in the case of the Lennard-Jones fluid we take $N = 640$ points such that $T_l/T_c = [1{,}1, 4.4]$ and $\varrho_l/\varrho_c \in [0{,}2.9]$. We now refit by linear regression these »experimental P, ϱ, T data« by four different ansatzes (4) to obtain four additional analytic expressions $P_k(\varrho, T)$, $k =$ II, III, VII, IX which presumably approximate the unknown equation of state of the Lennard-Jones fluid. The first three ansatzes, $k =$ II, III and VII, were obtained by modifying $P_{\mathrm{I}}(\varrho, T)$ by replacing $w_{\mathrm{I}}(\varrho) = \exp(-\gamma_{\mathrm{I}}\, \varrho^2)$ with various analytic expressions given in the second column of Table 1, choosing thereby γ_k so that the ratio $w_{\mathrm{I}}(\varrho)/w_k(\varrho)$ is of the same order of magnitude within the density interval considered; the last ansatz $k =$ IX was obtained from $P_{\mathrm{I}}(\varrho, T)$ by omitting nine terms. All four equations of state $P_k(\varrho, T)$, $k =$ II, III, VII and IX, reproduce *experimental data* P_l, ϱ_l, T_l with an accuracy comparable to that with which $P_{\mathrm{I}}(\varrho, T)$ reproduces the original P, ϱ, T data used to determine its constants. To get an idea of how much the accuracy of P, ϱ, T data affects the symmetries of the associated empirical equation of state, we generated two additional sets of statistically disturbed synthetic data, say $P_l(\varrho_l, T_l)(1 + \Delta_l)$ with Δ_l having random values between $\pm 10^{-3}$ and $\pm 10^{-2}$, respectively. Then we refitted these two sets of statistically perturbed data again with the original ansatz of $P_{\mathrm{I}}(\varrho. T)$ denoting the thus obtained empirical equations of state P_k as $k =$ Ia and IIb, respectively.

In order to get an idea of the symmetries of the P, ϱ, T surface of N_2 fluid, we will investigate Jacobsen and Stewart's[6] empirical equation of state, say

TABLE 1

k	$w(\varrho)$	$i =$	$2k+1 =$	Number of terms	Name — Descrip.
I	$\exp(-\gamma_I \varrho^2)$	$2, 3, \cdots, 9$	$3, 5, \cdots, 13$	$19 + 13 = 32$	Jacobsen & Stewart's
II	$\exp(-\gamma_{II} \varrho^3)$	$2, 3, \cdots, 9$	$3, 5, \cdots, 13$	$19 + 13 = 32$	Modified
III	$\exp(-\gamma_{III} \varrho^4)$	$2, 3, \cdots, 9$	$3, 5, \cdots, 13$	$19 + 13 = 32$	Jacobsen &
IV	$(1 + \gamma_{IV} \varrho^2)^{-1}$	$2, 3, \cdots, 9$	$3, 5, \cdots, 13$	$19 + 13 = 32$	Stewart's
V	$(1 + \gamma_V \varrho^3)^{-1}$	$2, 3, \cdots, 9$	$3, 5, \cdots, 13$	$19 + 13 = 32$	
VI	$(1 + \gamma_{VI} \varrho^4)^{-1}$	$2, 3, \cdots, 9$	$3, 5, \cdots, 13$	$19 + 13 = 32$	
VII	$(1 + \gamma_{VII} \varrho^6)^{-1}$	$2, 3, \cdots, 9$	$3, 5, \cdots, 13$	$19 + 13 = 32$	
VIII	$\exp(-\gamma_I \varrho^2)$	$2, 3, 4, 5, 7, 9$	$3, 5, 7, 11, 13$	$14 + 6 = 20$	Shortened
IX	$\exp(-\gamma_I \varrho^2)$	$2, 3, 4, 5, 8$	$3, 7, 9, 11. 13$	$15 + 8 = 23$	Jasobsen & Stewart's
X	$\exp(-\gamma_I \varrho^2)$	$2, 3, 4, 5, 6, 7, 8$	$3, 5, 7, 11, 13$	$17 + 8 = 25$	
XI	$\exp(-\gamma_{XI} \varrho^2)$	$2, 3, 4, 5, 6$	$3, 5$	$13 + 6 = 19$	Bender's
XII	$\exp(-\gamma_{XII} \varrho^2)$	$2, 3, \cdots, 8$	$3, 5, 7, 9, 11, 15$	$15 + 6 = 21$	de Reuch & Armstrong's
XIII	0	$2, 3, \cdots, 10$	—	$36 + 0 = 36$	Virial series
XIV	0	$2, 3, \cdots, 9$	—	$26 + 0 = 26$	

Schematic description of the variety of empirical equations of state $P_k(\varrho, T)$ studied, whose analytic expressions are of the form (4). The number of terms is given as the sum of the number of terms in the first and the second sum of (4).

$P_k(\varrho, T)$ with $k = \mathrm{I}$, since its ansatz equals that of the Lennard-Jones fluid. Again we generate 1273 synthetic data $P_l = P_I(\varrho_l, T_l)$, such that $\varrho_l/\varrho_c \in [0.2, 3.6 - 0.7(T/T_c - 2)/4]$ if $T_l/T_c \in [2,6]$ and $\varrho_l/\varrho_c \in [0.2, 1 - 0.1(T/T_c - 6)]$ if $T_l/T_c \in (6, 9)$.

Refitting them we construct seven additional empirical equations of state $P_k(\varrho, T)$, $k = $ II, III, IV, V, VI, VIII and X, so that altogether we can study eight analytically different approximations to the P, ϱ, T surface of N_2 fluid.

To detect the possible symmetries in question of the P, ϱ, T surface of a xenon fluid, we will consider the virial equation of state, say $P_{XIII}(\varrho, T)$, used by Juza and Šifner[7] to represent available experimental P, ϱ, T data. Again we generated 1052 synthetic experimental data $P_l = P_{XIII}(\varrho_l, T_l)$ such that $\varrho_l/\varrho_c \in [0.3, 3.3 - 1.5(T/T_c - 1.5)]$ and $T_l/T_c \in [1.5, 3.5]$, and used them to realize six additional empirical equations of state $P_k(\varrho, T)$, $k = $ I, II, III, IV, V and VI; thereby we put $\gamma_I = \varrho_c^{-2}$ as suggested by Bender, and chose the rest of γ_k' s so that the ratio $w_k(\varrho)/w_I(\varrho)$ is of the same order for all densities ϱ considered.

We will consider symmetries of the P, ϱ, T surface of argon by studying the virial equation of state, say $P_{XIV}(\varrho, T)$ provided by Vasserman and Krejzerova[8].

Teja and Singh[9] used Bender's type of empirical equation, say $P_{XI}(\varrho, T)$, to represent the experimental data of some n-alkanes. We will use their results to study symmetries of ethane, propane and n-pentane.

We study the properties of ethylene using Bender's[10] empirical equation $P_I(\varrho, T)_I$. The properties of propylene will be studied using the empirical equation, say $P_{XII}(\varrho, T)$, provided by Angus, Armstrong and de Reuck[11].

Altogether we will consider nine substantially different fluids and a variety of 14 analytically distinct empirical equations of state so as to make sure that our conclusions obout the symmetric properties of P, ϱ, T surfaces will not be erroneously based on fortuitous observations of some peculiar property of the particular empirical equation employed to represent experimental P, ϱ, T data.

The main purpose of an empirical equation, say $P_I(\varrho, T)$ the Lennard-Jones fluid, is interpolation of those experimental P, ϱ, T data which were used to determine constants a_{ij} and b_{ij} of the ansatz (4) used. In general, one does not employ an empirical equation of state $P_I(\varrho, T)$ for extrapolating experimental data, since one does not expect $P_I(\varrho, T)$ to yield satisfactory approximations to the true pressure $P(\varrho, T)$ of the Lennard-Jones fluid for densities ϱ and temperatures T outside the ϱ, T domain of the experimental data used. In particular, if T_{max} is the highest temperature of the P, ϱ, T data used, then one would not expect isothermal behaviour of $P_I(\varrho, T)$ to aproximate that of $P(\varrho, T)$ for $T \gg T_{max}$.

For empirical equations of the fluids we will investigate, the maximal temperatures of experimental data used are as follows: $T_{max} = 4.4\, T_c$ in the case of the Lennard-Jones fluid; $T_{max} = 8.5\, T_c$ for N_2 fluid; $T_{max} = 2.5\, T_c$ for Xe; $T_{max} = 7\, T_c$ for argon; $T_{max} = 3.3\, T_c$ for ethane; $T_{max} = 3.1\, T_c$ for propane; $T_{max} = 2.6\, T_c$ for n-pentane; $T_{max} = 1.5\, T_c$ for ethylene; and $T_{max} = 1.6\, T_c$ for propylene. Our investigations will bring forth the surprising fact that some of the empirical equations $P_k(\varrho, T)$ considered do exibit certain symmetric properties also for much higher isotherms T than the associated maximal temperature T_{max} of the experimental data used in determining their constants.

b) *Analysis of experimental data*

First we consider local isothermal antisymmetry of the chemical potential μ of the Lennard-Jones fluid in the vicinity of the critical density ϱ_c. Second isothermal derivatives $\partial^2 \mu_k(\varrho, T)/\partial \varrho^2$ computed from all five empirical equations $P_k(\varrho, T)$ of the Lennard-Jones fluid display a zero, say $\varrho_\mu^{(2)}(T) \approx \varrho_c$ for temperatures up to three times greater than the maximal temperature of the experimental data reproduced by $P_k(\varrho, T)$. For k = I, II, III and VII we have plotted this zero $\varrho_\mu^{(2)}(T)$ versus $T/T_c \in [1, 14]$ in Fig. 1. Further, the chemical potentials μ_{Ia} and μ_{Ib} associated by (1) with empirical equations of state P_{Ia} and P_{Ib} representing statistically perturbed data also display the same degree of antisymmetry in the vicinity of the critical density, cf. Fig. 1. These results show that the chemical potential of the model fluid whose behaviour has been determined by computer simulation also displays the same kind of antisymmetry in the vicinity of the critical density as the real fluids considered[3]. For comparison we give in Fig. 2 some new corresponding results about argon, nitrogen, propane and ethane. Previous investigations of the chemical potential μ of certain real fluids[3] gave indications for the possibility that also $\partial^4 \mu(\varrho, T)/\partial \varrho^4$ may have a temperature independent zero in the vicinity of the critical density ϱ_c; Fig. 2 gives such indications in the case of ethane fluid.

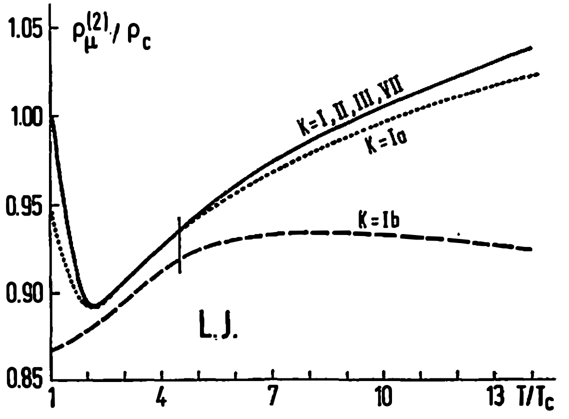

Fig. 1. The normalized zero $\varrho_\mu{}^{(2)}/\varrho_c \in [0.85, 1.05]$ of the second isothermal derivative of the chemical potential $\mu_k(\varrho, T)$ of the Lennard-Jones fluid is plotted versus $T/T_c \in [1, 14]$. The vertical line at $T/T_c = 4.4$ indicates the high temperature boundary T_{max} of *experimental* P, ϱ, T data used in determining empirical equations of state $P_k(\varrho, T)$, $k =$ I, Ia, Ib, II, III, VII, of the Lennard-Jones fluid.

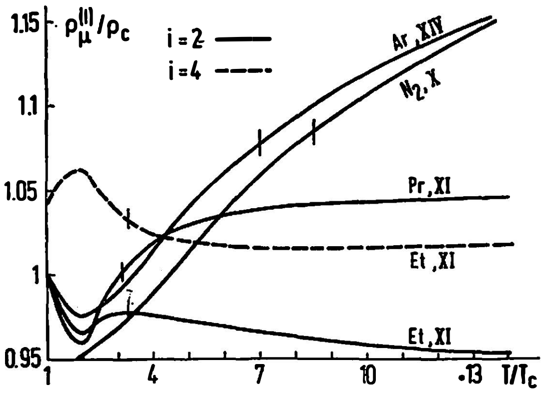

Fig. 2. The normalized zeros $\varrho_\mu{}^{(i)}/\varrho_c \in [0.95, 1.15]$ of $\partial^i \mu_k(\varrho, T)/\partial\varrho^i$, $i = 2, 4$, of argon, $k =$ = XIV, nitrogen, $k =$ X, propane, $k =$ XI, and ethane, $k =$ XI, are plotted versus $T/T_c \in [1, 14]$. Vertical lines indicate corresponding values of T_{max}.

Next we checked whether the empirical equations $P_k(\varrho, T)$, $k =$ I, Ia, Ib, II, III, VII and IX, of the Lennard-Jones fluid indicate the existence of some symmetry of the chemical potential μ within the density interval $[2.4\,\varrho_c, 3\,\varrho_c]$. We found that the fourth isothermal derivatives $\partial^4\mu_k(\varrho, T)/\partial\varrho^4$ of the approximations $\mu_k(\varrho, T)$, $k =$ Ia, Ib, II, III, VII and VIII to the chemical potential $\mu(\varrho, T)$ of the Lennard-Jones fluid do have zeros, say $\varrho_\mu^{(4)}(T) \in [2.4\,\varrho_c, 3\,\varrho_c]$ over the whole temperature interval $T/T_c \in [1, 14]$. An analogous property is also displayed for high temperatures by the following empirical equations $P_k(\varrho, T)$, $k =$ VIII, X of N_2 fluid, and k = XIII and III of Xe fluid, Fig. 3, and also by P_{XII} of propylene up to 2.6 T_c. Moreover, empirical equations P_{VII} of the Lennard-Jones fluid and P_X of N_2 fluid provide such approximations to the chemical potentials whose isothermal derivatives $\partial^i \mu_k (\varrho, T)/\partial \varrho^i$, $i = 4, 6, 8, 10$, have zeros $\varrho_\mu^{(i)}$, $i =$

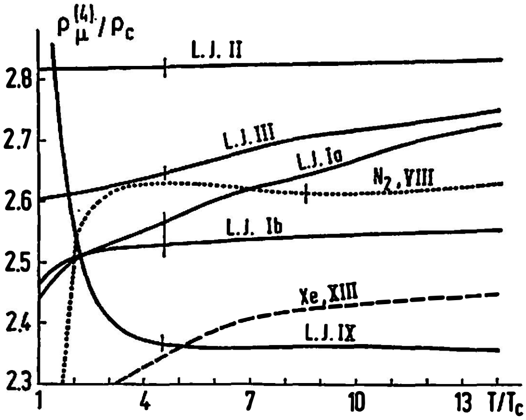

Fig. 3. The normalized zeros $\varrho_\mu^{(2)}/\varrho_c \in [2.3, 2.85]$ of the fourth isothermal derivatives of the chemical potential $\mu_k (\varrho, T)$ of the Lennard-Jones, N_2 and Xe fluids are plotted versus $T/T_c \in$ $\in [1, 14]$ for k = I*a*, I*b*, II, III, IX, k = VIII and XIII, respectively.

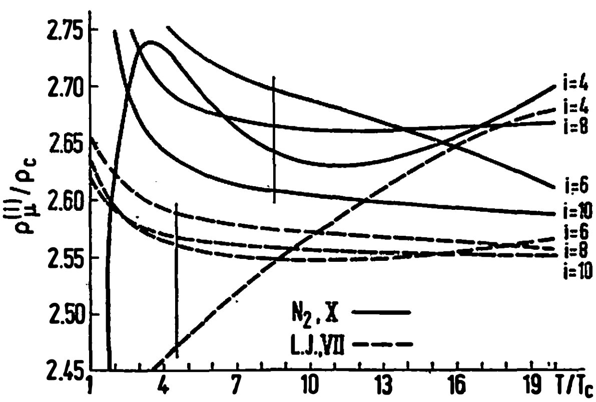

Fig. 4. The normalized zeros $\varrho_\mu^{(i)}/\varrho_c \in [2.45, 2.75]$ of $\partial^i \mu_k/\partial \varrho^i$, $i = 4, 6, 8, 10$, plotted versus $T/T_c \in [1, 14]$ for the empirical equations of state $P_k (\varrho, T)$, of the Lennard-Jones and N_2 fluids where k = VII and X, respectively.

$= 4, 6, 8, 10$, within the density interval $[2.4\, \varrho_c, 3\, \varrho_c]$ for all $T/T_c \in [3, 14]$, Fig. 4. These results indicate the hitherto unknown possibility that also $\partial^2 \mu/\partial \varrho^2$ of the Lennard-Jones and of some real fluids could be strongly antisymmetric along a density line $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\, \varrho_c$, at least for higher temperatures. In Fig.5

we have plotted for the 2 T_c isotherm the normalized values $\varrho_c^5 P_c^{-1} \partial^4 \mu_k/\partial\varrho^4$ of the fourth derivative of the approximate chemical potentials μ_k of the Lennard-Jones, nitrogen and propylene fluids to point out the surprising fact that they all display a zero within the density interval [2.4 ϱ_c, 3 ϱ_c], though their ϱ-dependences are both quantitatively and qualitatively markedly different, so much so that we have to use a logarithmic scale.

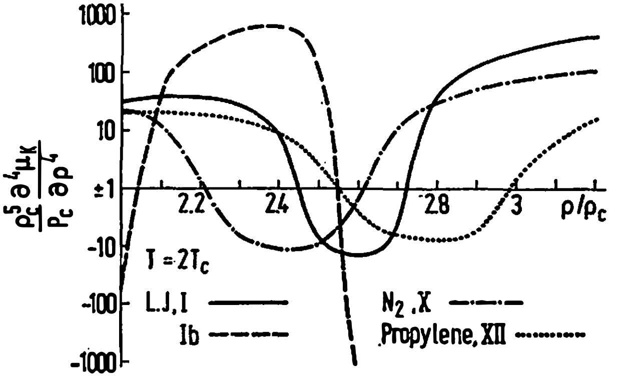

Fig. 5. The normalized values of $\partial^4\mu_k/\partial\varrho^4$ are plotted on a logarithmic scale versus $\varrho/\varrho_c \in [2, 3.2]$ for 2 T_c isotherms of the Lennard-Jones, k = I and Ib; N_2, k = X; and propylene, k = XII, fluids.

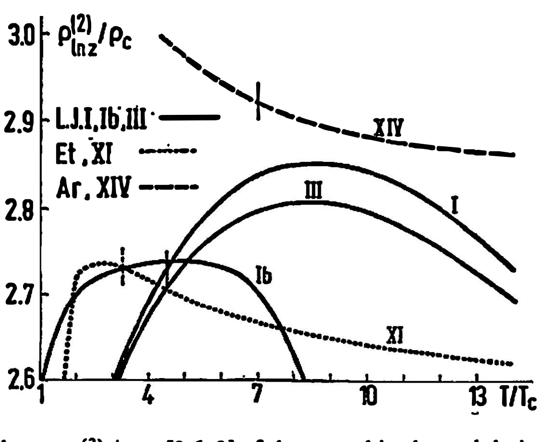

Fig. 6. The normalized zeros $\varrho_{\ln z}^{(2)}/\varrho_c \in [2.6, 3]$ of the second isothermal derivative of ln $(P_k/T\varrho R)$ are plotted versus $T/T_c \in [1, 14]$ for the Lennard-Jones, k = I, Ib and III, ethane, k = XI, and argon, k = XIV, fluids.

Next we investigated the approximations ln $(P_k(\varrho, T)/\varrho RT)$, k = I, II, III, VII and IX, to the logarithm of the compressibility of the Lennard-Jones fluid and their first nine isothermal derivatives in the vicinity of $\varrho = \varrho_c$ and $\varrho = 2.7\,\varrho_c$. We found that at higher temperatures their second isothermal derivatives do have zeros, say $\varrho_{\ln z}^{(2)}(T) \in [2.6\,\varrho_c, 2.9\,\varrho_c]$; cf. Fig. 6 where for comparison we have plotted some new results for ethane and argon fluids. The fact that the second isothermal derivative of $\ln z_I$, $z_I \equiv P_I(\varrho, T)/\varrho RT$ has a zero in the vicinity of, say $\varrho = \varrho_{ac} = 2.75\,\varrho_c$ indicates local antisymmetry of $\ln z_I$ along the density line $\varrho = \varrho_{ac} = 2.75\,\varrho_c$. The following expression

$$\Delta_{ac}(\varrho_{ac}, |\varrho - \varrho_{ac}|, T) \equiv |1 - z_I^2(\varrho_{ac}, T)\, z_I^{-1}(\varrho_{ac} + |\varrho - \varrho_{ac}|, T)\, z_I^{-1}(\varrho_{ac} - |\varrho - \varrho_{ac}|, T)| \qquad (5)$$

gives a quantitative global measure of this antisymmetry along the density line $\varrho = \varrho_{ac}$[4].

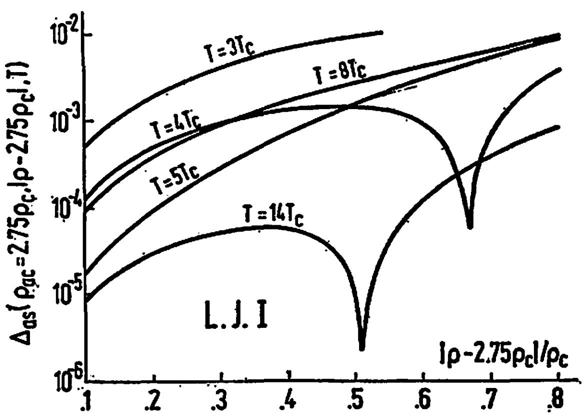

Fig. 7. For isotherms $T/T_c = 3, 4, 5, 8, 14$ of the Lennard-Jones fluid the measure of antisymmetry $\Delta_{as}(\varrho_{ac}, |\varrho - \varrho_{ac}|, T)$ of $\ln(P_{k=I}/RT\varrho)$ around $\varrho = \varrho_{ac} = 2.75\,\varrho_c$ is plotted on a logarithmic scale as a function of $|\varrho - \varrho_{ac}|/\varrho_c \in [0.1, 0.8]$.

We have plotted the values of Δ_{ac} versus $|\varrho - 2.75\,\varrho_c|/\varrho_c$ for different isotherms in Fig. 7, which indicates that for isotherms $T/T_c \in [3, 14]$ the values of $z_I(\varrho, T)$ need to be altered by only up to 0.3% to make $\ln z_I$ completely antisymmetric around the density line $\varrho = \varrho_{ac} = 2.75\,\varrho_c$ for $|\varrho - 2.75\,\varrho_c| < 0.5\,\varrho_c$; this required modification of the values of $z_I(\varrho, T)$ is comparable to the estimated accuracy of the P, ϱ, T data represented by $z_I(\varrho, T)$.

3. *Symmetries of the isothermal P, ϱ dependence*

To investigate possible symmetries of the isothermal derivatives $\partial^i P(\varrho, T)/\partial\varrho^i$ of the Lennard-Jones fluid we computed for sixty isotherms $T \in (0, 14\,T_c)$ the numerical values of the first ten isothermal derivatives $\partial^i P_k(\varrho, T)/\partial\varrho^i$, $\varrho \in [0, 6\,\varrho_c]$, of the seven approximations $P_k(\varrho, T)$, k = I, Ia, Ib, II, III, VII and IX, to the equation of state of the Lennard-Jones fluid. Thereby we were looking for such zeros $\varrho^{(i)}(T)$ of $\partial^i P_k/\partial\varrho^i$, $i = 1, 2, \ldots, 10$, which stay in the vicinity of the critical density or 2.7 times the critical density for all computed isotherms. We found that the sixth, eighth and tenth partial derivatives $\partial^i P_k/\partial\varrho^i$ of all approximations considered with the exception of k = Ib and k = IX have such zeros in the vicinity of the critical density, Fig. 8. Furthermore, approximations k = I, II, VII

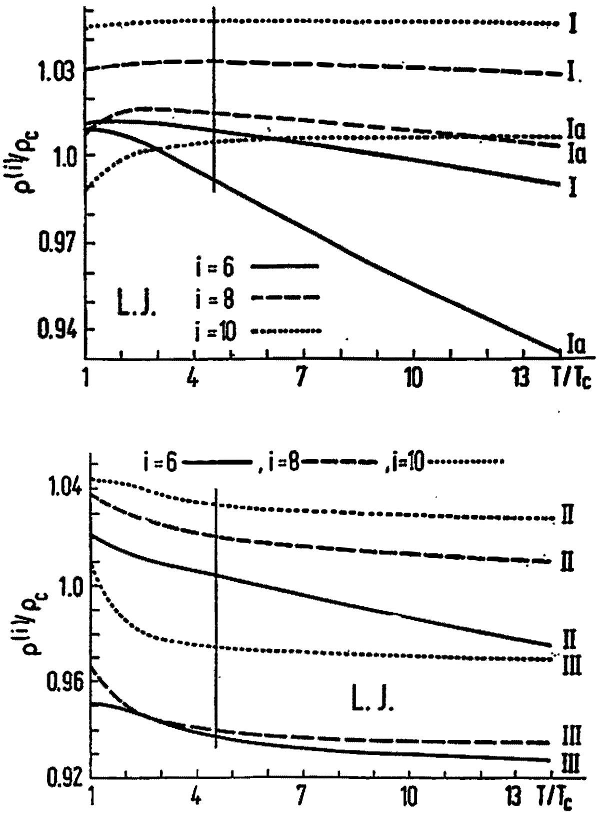

Fig. 8. For the Lennard-Jones fluid the normalized zeros $\varrho^{(i)}/\varrho_c \approx 1$, $i = 6, 8, 10$ of $\partial^i P_k(\varrho, T)/\partial\varrho^i$ with k = I, I*a*, II, III, are plotted versus $T/T_c \in [1, 14]$.

and IX also display an analogous property within the density interval $[2.4\,\varrho_c, 3\,\varrho_c]$, Fig. 9. These results indicate the possibility that the fourth isothermal partial derivative $\partial^4 P(\varrho, T)/\partial\varrho^4$ of the pressure of the Lennard-Jones fluid may be strongly antisymmetric along the density lines $\varrho = \varrho_{cc} = (1 \pm 0.1)\,\varrho_c$ and $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\,\varrho_c$. We note that ansatzes $P_k(\varrho, T)$ considered cannot simultaneously satisfy conditions $\partial^i P_k/\partial\varrho^i = 0$, $i = 6, 8, 10$, for all temperatures at two temperature independent densities, which gives an additional indication that the observed local antisymmetries of $\partial^4 P_k/\partial\varrho^4$ are effected by an intrinsic physical property of the Lennard-Jones fluid.

To get on indication of the degree of antisymmetry of the fourth isothermal derivative of the pressure of the Lennard-Jones fluid around the density lines $\varrho = \varrho_{cc}$ and $\varrho = \varrho_{ac}$, we calculated the temperature dependence of the eight zeros $\varrho(T)$ of $\partial^i P_k/\partial\varrho^i$, $i = 6, 8, 10, \ldots, 20$, closest to the densities ϱ_c and $2.7\,\varrho_c$ for

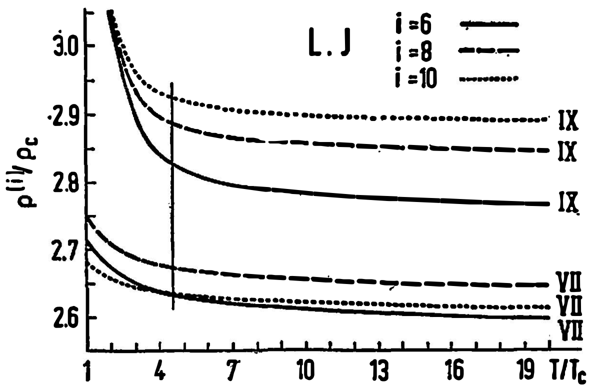

Fig. 9. For the Lennard-Jones fluid the normalized zeros $\varrho^{(6)}/\varrho_c$, $\varrho^{(8)}/\varrho_c$ and $\varrho^{(10)}/\varrho_c \in [2.55, 3.05]$ of the sixth, eight and tenth isothermal derivative of $P_k(\varrho, T)$ with respect to density ϱ, k = VII and IX, are plotted versus $T/T_c \in [1, 20]$.

k = I, III, and VII and $T/T_c \in [1, 20]$. Horizontal dashes in Fig. 10 indicate the range of values the zeros $\varrho^{(i)}(T)$ assume for temperatures $T/T_c \in [1, 20]$. The results of Fig. 10 strongly suggest the possibility that for any temperature the derivative $\partial^4 P/\partial \varrho^4$ of the Lennard-Jones fluid is actually completely antisymmetric around two density lines $\varrho = \varrho_{cc} = (1 \pm 0.1)\,\varrho_c$ and $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\,\varrho_c$. We will investigate this possibility further in a subsequent paper.

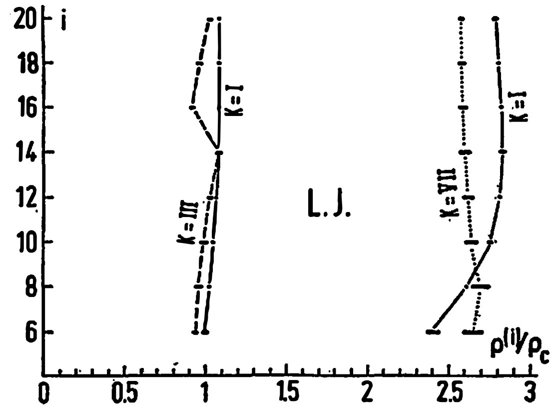

Fig. 10. For the Lennard-Jones fluid we have indicated the range of zeros $\varrho^{(i)}(T) \approx \varrho_c$ and $\varrho^{(i)}(T) \approx 2.7\,\varrho_c$ of $\partial^i P_k(\varrho, T)/\partial \varrho^i$, $i = 6, 8, 10, \cdots, 20$, k = I, III, VII, within the temperature interval $T/T_c \in [1,20]$ using horizontal dashes. Full, dashed and dotted vertical lines connect ranges of zeros $\varrho^{(i)}(T)$, $T/T_c \in [1, 20]$, corresponding to state equations k = I, III and VII, respectively.

In Fig. 11 we have plotted on a logarithmic scale versus $\varrho/\varrho_c \in [0, 3]$ the normalized values of the sixth isothermal derivative $\partial^6 P_k/\partial \varrho^6$ for three different approximations k = II, III, VII so as to show that their values differ up to two orders of magnitude as expected, yet surprisingly exhibit very close zeros near ϱ_c and 2.6 ϱ_c. This fact supports the hypothesis that the antisymmetry of $\partial^4 P/\partial\varrho^4$ of the Lennard-Jones fluid is a physical property much more stable against small experimental inaccuracies than the values of $\partial^4 P/\partial\varrho^4$ themselves.

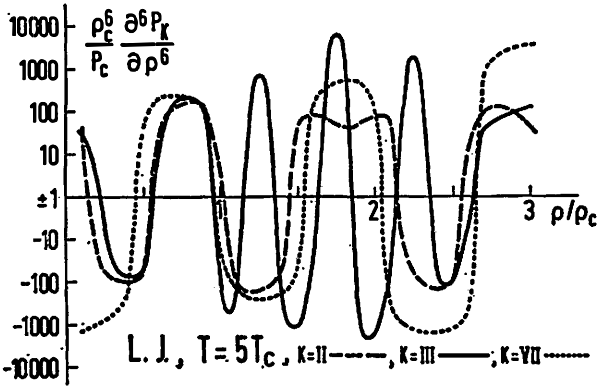

Fig. 11. For the 5 T_c isotherm of the Lennard-Jones fluid, the normalized values of isothermal derivatives $\varrho_c^6 P_c^{-1} \partial^6 P_k(\varrho, T)/\partial\varrho^6$ with k = II, III and VII, plotted versus $\varrho/\varrho_c \in [0,3]$.

If the hypothetical antisymmetry of $\partial^4 P/\partial\varrho^4$ of the model Lennard-Jones fluid is a physical property not particular to the Lennard-Jones potential, it makes sense to check whether empirical equations of state of real fluids also display analogous properties. First we investigated equations of state $P_k(\varrho, T)$ of N_2 fluid and found that the derivatives $\partial^6 P_k/\partial\varrho^6$, k = II, III, V, VI, VIII, do have zeros $\varrho^{(6)}(T) \approx \varrho_c$ for $T \in [T_c, 14\,T_c]$, Fig. 12. Moreover, the higher derivatives $\partial^8 P_k/\partial\varrho^8$

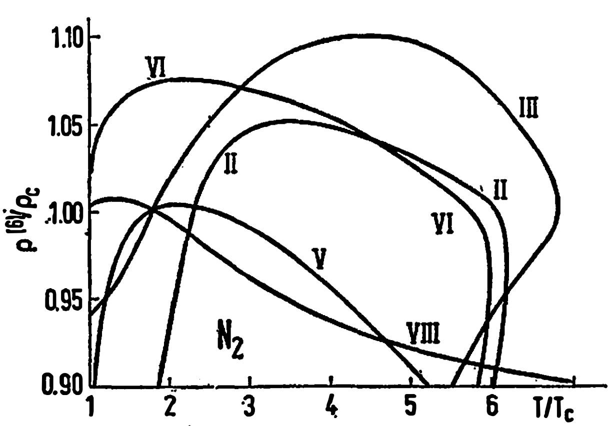

Fig. 12. The normalized zero $\varrho^{(6)}/\varrho_c \in [0.9, 1.1]$ of $\partial^6 P_k(\varrho, T)/\partial\varrho^6$ is plotted versus $T/T_c \in [1,7]$ for empirical equations of state k = II, III, V, VI and of VIII N_2 fluid.

and $\partial^{10}P_k/\partial\varrho^{10}$ of equations k = V and k = VIII also have zeros near the critical density ϱ_c for $T \in [T_c, 14\,T_c]$, Fig. 13. Within the density interval $[2.7\,\varrho_c, 3\,\varrho_c]$ the equations k = III, VIII and X are such that their derivatives $\partial^i P_k/\partial\varrho^i$, $i =$ $= 6, 8, 10$, have zeros there for $T \in [T_c, 14\,T_c]$, Fig. 14.

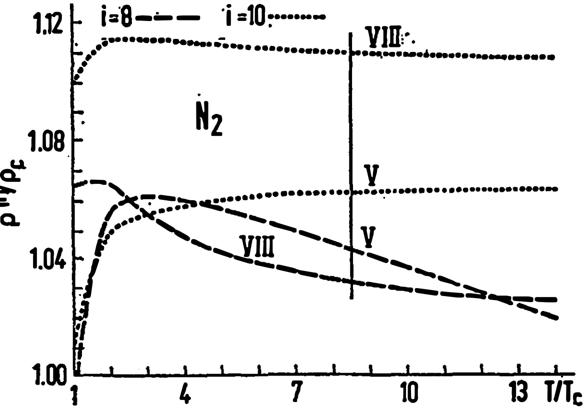

Fig. 13. For empirical equations k = V and VIII of N_2 fluid the normalized zeros $\varrho^{(i)}/\varrho_c \in [1, 1.12]$, $i = 8, 10$, of $\partial^i P_k(\varrho, T)/\partial\varrho^i$ are plotted versus $T/T_c \in [1, 14]$.

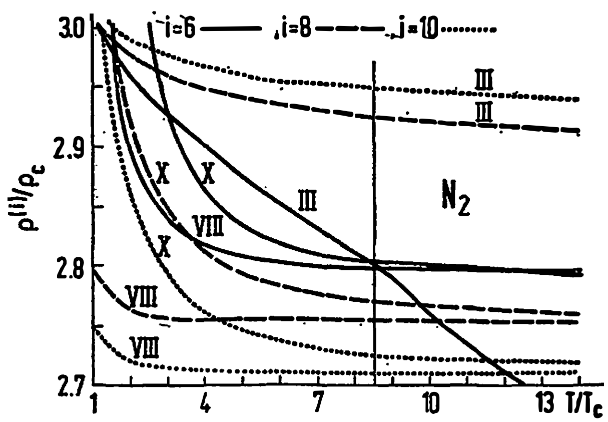

Fig. 14. For empirical equations of state k = III, VIII and X of N_2 fluid we have plotted the normalized zeros $\varrho^{(i)}/\varrho_c \in [2.7, 3]$, $i = 6, 8, 10$ of $\partial^i P_k/\partial\varrho^i$.

For the 5 T_c isotherm of N_2 fluid Fig. 15 again demonstrates the fact that though the isothermal dependences of $\partial^6 P_k(\varrho, 5\,T_c)/\partial\varrho^6$, k = III, IV, VI, VIII, differ substantially, their zeros in the vicinity of $\varrho = 2.8\,\varrho_c$ almost coincide.

Next we investigated empirical equations k = I, II, III, IV, V, VI and XIII of Xe fluid for above critical isotherms up to 14 T_c. We found that their isothermal derivatives $\partial^6 P_k/\partial\varrho^6$ with the exception of k = II have slightly temperature dependent zeros in the vicinity of the critical density, but not so within the density interval $[2.4\,\varrho_c, 3\,\varrho_c]$; further, $\partial^8 P_k/\partial\varrho^8$, for $k =$ I, III, V, VI, XIII and $\partial^{10} P_k/\partial\varrho^{10}$ for $k =$ I, V, VI also have zeros in the vicinity of the critical density ϱ_c.

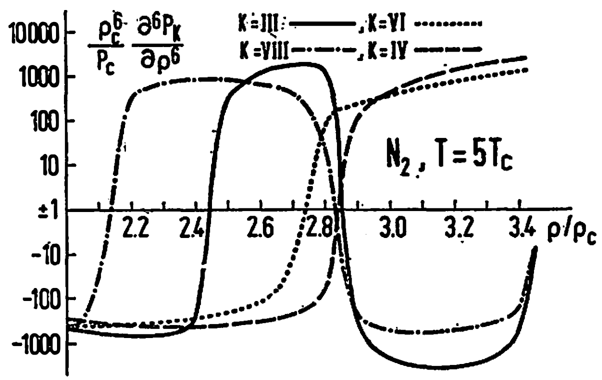

Fig. 15. For the $T = 5\,T_c$ isotherm of N_2 fluid the values of $\varrho^6\, P_c^{-1}\, \partial^6 P_k/\partial\varrho^6$ computed from empirical equations of state $P_k(\varrho, T)$, $k =$ III, IV, VI and VIII, are plotted versus $\varrho/\varrho_c \in [2, 3.4]$ on a logarithmic scale.

The virial empirical equation $P_{\rm XIV}$ for argon is such that its sixth partial isothermal derivative has a slightly temperature dependent zero in the vicinity of the critical density (but not so near $2.7\,\varrho_c$) for above critical temperatures up to $14\,T_c$, cf. Fig. 16.

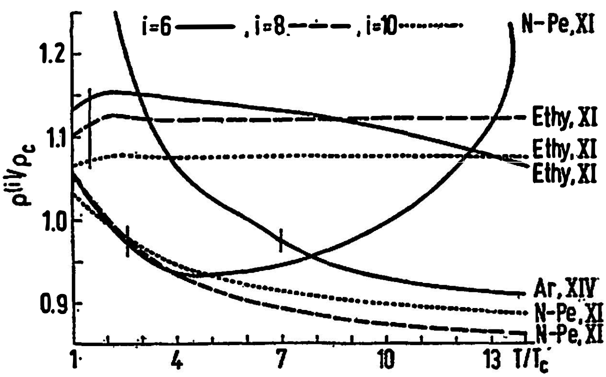

Fig. 16. The normalized zeros $\varrho^{(i)}/\varrho_c \in [0.85, 1.25)$, $i = 6, 8, 10$, of $\partial^i P_k(\varrho, T)/\partial\varrho^i$ for empirical equations of state $P_k(\varrho, T)$ of n-pentane, $k =$ XI, ethylene, $k =$ XI, and argon, $k =$ XIV, are plotted versus $T/T_c \in [1, 14]$.

In the case of ethane and propane $\partial^6 P_{\rm XI}/\partial\varrho^6$ does not have slightly temperature dependent zeros in the vicinity of ϱ_c or $2.7\,\varrho_c$, whereas the same kind of empirical equation $P_{\rm XI}$ for n-pentane and ethylene is such that its derivatives $\partial^i P_{\rm XI}/\partial\varrho^i$, $i = 6, 8, 10$, do have zeros in the vicinity of ϱ_c for $T \in [T_c, 14\,T_c]$, cf. Fig. 16, and in the case of n-pentane also in the vicinity of $2.7\,\varrho_c$ up to $5\,T_c$. In the case of propylene fluid $\partial^6 P_{XII}/\partial\varrho^6$, $\partial^8 P_{XII}/\partial\varrho^8$ and $\partial^{10} P_{XII}/\partial\varrho^{10}$ do have zeros in the vicinity of 2.5 ϱ_c for $T \in [T_c, 14\ T_c]$, but there are no zeros in the vicinity of ϱ_c.

Altogether the results of this section show that many of the experimentally determined P, ϱ, T surfaces of the Lennard-Jones and of the few real fluids considered are such that their fourth isothermal derivatives of pressure are antisymmetric in the vicinity of the densities ϱ_c and 2.7 ϱ_c. In the case of the Lennard-Jones fluid empirical equations P_{Ia} and P_{Ib} point out that when the inaccuracy of experimental data exceeds a few percent, the corresponding empirical equation of state may not exhibit such antisymmetries; this may account for these antisymmetries being more pronounced in the case of the Lennard-Jones fluid as compared to the other fluids considered.

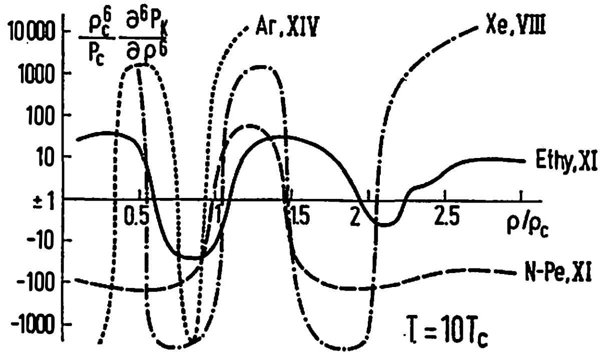

Fig. 17. For the $T = 10\ T_c$ isotherms of empirical equations of state $P_k(\varrho, T)$ of ethylene k = XI, n-pentane, k = XI, xenon VIII, and argon, k = XIV, the corresponding $\varrho^6 P_c^{-1}\, \partial^6 P_k/\partial\varrho^6$ values are plotted on a logarithmic scale versus $\varrho/\varrho_c \in [0, 3]$.

In Fig. 17 we have plotted isothermal dependences of the sixth derivative $\partial^6 P_k/\partial\varrho^6$ of the extrapolated pressure of four different real fluids. Not unexpectedly, the values of these various derivatives $\partial^6 P_k/\partial\varrho^6$ plotted have nothing in common but the remarkable fact of all being zero in the vicinity of the critical density ϱ_c, and where the most extrapolated pressure $P_{XI}(\varrho, 10\ T_c)$ of n-pentane (where $10\ T_c/T_{max}$ equals almost four), though being negative for all densities, still displays local antisymmetry of its fourth isothermal derivative in the vicinity of ϱ_c.

4. *Discussion*

An exact P, ϱ, T surface is as yet not known for any realistic model fluid, and in principle imposible to know for any real fluid. So we can study properties of P, ϱ, T surfaces of realistic model and real fluids only by proxy, considering various approximations. Investigating approximate P, ϱ, T surfaces of the model Lennard-Jones and of some real fluids as described by various kinds of empirical equations of state, we have presented in this and preceding papers[3,4] experimental evidence suggesting that were the pressure $P(\varrho, T)$ of these fluids known exactly we could observe over a wide, above critical temperature interval some or all of the following stable physical properties:

1. One or more even isothermal derivatives of pressure have zeros within the density intervals $[0.9\ \varrho_c, 1.1\ \varrho_c]$ and $[2.4\ \varrho_c, 3\ \varrho_c]$, i. e. there are slightly temperature dependent functions, say $\varrho_{cc}^{(i)}(T) \in [0.9\ \varrho_c, 1.1\ \varrho_c]$ and $\varrho_{ac}^{(i)}(T) \in [2.4\ \varrho_c, 3\ \varrho_c]$ such that

$$\partial^i P(\varrho, T)/\partial \varrho^i = 0 \text{ at } \varrho = \varrho_{cc}^{(i)}(T) \text{ and } \varrho = \varrho_{ac}^{(i)}(T) \tag{6}$$

where $i = 6, 8, \ldots, i_{max}$.

2. Second and/or fourth isothermal derivatives of the associated chemical potential μ equal zero in the vicinity of the critical density, and/or in the vicinity of $\varrho = 2.7\ \varrho_c$, i. e. there are up to three slightly temperature dependent functions, say

$$\varrho_{\mu cc}^{(2)}(T),\ \varrho_{\mu cc}^{(4)}(T) \in [0.9\ \varrho_c, 1.1\ \varrho_c] \text{ and } \varrho_{\mu ac}^{(4)} \in [2.4\ \varrho_c, 3\ \varrho_c] \text{ such that}$$

$$\partial^2 \mu\,(\varrho = \varrho_{\mu cc}^{(2)}, T)/\partial \varrho^2 = 0,\ \partial^4 \mu\,(\varrho = \varrho_{\mu cc}^{(4)}, T)/\partial \varrho^4 = 0 \tag{7}$$

and

$$\partial^4 \mu\,(\varrho = \varrho_{\mu ac}^{(4)}, T)/\partial \varrho^4 = 0. \tag{8}$$

3. Second and possibly also higher derivatives of the logarithm of the compressibility factor $z = P/R\varrho T$ have zeros along the density line $\varrho = \varrho_{ac} \approx 2.7\ \varrho_c$, i. e. there are such slightly temperature dependent functions, say $\varrho_{\ln z}^{(j)}(T) \in$ $\in [2.4\ \varrho_c, 3\ \varrho_c]$ such that

$$\partial^j \ln z\,(\varrho = \varrho_{\ln z}^{(j)}, T)/\partial \varrho^j = 0 \tag{9}$$

for $j = 2, 4, \ldots, j_{max}$.

These properties observed on some approximate P, ϱ, T surfaces of a model and on few real fluids indicate the need for physically realistic model fluids whose P, ϱ, T surfaces would exhibit two lines of antisymmetry, say $\varrho = \varrho_{cc} = (1 \pm$ $\pm\ 0.1)\ \varrho_c$ and $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\ \varrho_c$ along which they would display some or all of the following properties

$$\partial^i P/\partial \varrho^i = 0,\ i = 2, 4, \ldots, i_{max} \tag{10}$$

$$\partial^2 \mu/\partial \varrho^2 = 0, \tag{11}$$

$$\partial^4 \mu/\partial \varrho^4 = 0, \tag{12}$$

$$\partial^j \ln (P/\varrho RT)/\partial \varrho^j = 0,\ j = 2, 4, \ldots, j_{max}. \tag{13}$$

The results of this and the preceding papers[3,4] indicate that these properties of P, ϱ, T surfaces of such model fluids are most likely to be topological properties, preserved under sufficiently small deformations of P, ϱ, T surfaces, which can be, therefore, considered as physical characteristics. Such model fluids would help us in looking for a most general class of model fluids exhibiting exactly these antisymmetries, their common properties being the physical principles — laws — which imply these antisymmetries. In this way we would gain physical insight into the origin of the observed approximate antisymmetries of the fluids considered. Each such model fluid having a number of free parameters, its P, ϱ, T surface could be used for fitting experimental P, ϱ, T data, thereby automatically satisfying certain antisymmetric laws (10, 11, 12, 13); and the best obtainable fit of such an ansatz would give us a physical measure of how realistic is the model fluid considered.

The fact that some empirical equations of the fluids considered approximately satisfy relations (10, 11, 12, 13) suggests the possible existence of analytic ansatzes satisfying certain of these relations exactly, and efficient in fitting P, ϱ, T data of fluids. Efficient here means either that, in comparison with ansatzes having the same number of adjustable constants and not satisfying some of relations (10,11, 12, 13) automatically, they are able to fit given P, ϱ, T data with greater accuracy, or that they are able to effect fits of required accuracy with less constants than analogous ansatzes not displaying such antisymmetries automatically. Thereby it would be of interest to obtain an estimate of how accurately the most efficient ansatz, satisfying certain of the relations (10, 11, 12, 13) automatically, can fit the exact P, ϱ, T surfaces of real fluids, since this optimal accuracy can be considered as the accuracy with which real fluids obey these particular antisymmetry laws.

Inspecting the given plots of zeros $\varrho_{\mu}^{(i)}(T)$, $\varrho_{\ln z}^{(i)}(T)$ and $\varrho^{(i)}(T)$ of the approximations to the chemical potential, logarithm of the compressibility factor and pressure of the fluids considered, one gets an overall impression that in general they tend to be less temperature dependent at higher temperatures, say $T > 4\,T_c$, than they are at above-critical temperatures, say $T \in [T_c, 4\,T_c]$. A way to explain this fact could be as follows: These is a consensus[12] that the pressure P of real fluids as a function of their density ϱ and temperature T can be written as a sum of two functions, say

$$P(\varrho, T) = P_{cl}(\varrho, T) + P_{cr}(\varrho, T). \tag{14}$$

Expression $P_{cl}(\varrho, T)$, describing a classical mean field part of the pressure, is an analytic function of real fluid densities ϱ and of positive temperatures T, and the same goes for expression $P_{cr}(\varrho, T)$ but at the critical point $\varrho = \varrho_c$, $T = T_c$ where $P_{cr}(\varrho, T)$ has branch points described by the so-called critical exponents, e. g. for the critical isotherm we have

$$|P_{cr}(\varrho, T) - P_{cr}(\varrho_c, T_c)| \cong |\varrho - \varrho_c|^{\delta} \tag{15}$$

with $\delta \approx 4.2 - 5$. Expression $P_{cr}(\varrho, T)$ gives the part of the pressure effected by fluctuations, and so $|P_{cr}(\varrho, T)| \ll P_{cl}(\varrho, T)$ outside the critical region $\varrho \approx \approx \varrho_c$ and $T \approx T_c$. As a consequence, outside the critical region the experimental P, ϱ, T data of real fluids can be well represented by a suitable analytic ansatzes, e. g. $P(\varrho, T)$ as defined by (4).

As we pointed out before[3], according to Thom's theory of catastrophes one can expect the classical part $P_{cl}(\varrho, T)$ of pressure P to satisfy relations such as (10, 11, 12, 13) exactly at the critical density, say $\varrho = \varrho_{cc} \approx \varrho_c$, the fluid would have in the absence of fluctions. If it were actually so, these antisymmetries of $P_{cl}(\varrho, T)$ being stable physical properties by Thom's theory of catastrophes, the empirical equations of state $P_k(\varrho, T)$ would also tend te exhibit these antisymmetries, the more so the better they approximate the classical part $P_{cl}(\varrho, T)$ of P. Now $P_k(\varrho, T)$'s by fitting P, ϱ, T data are approximations to the whole pressure $P(\varrho, T)$ and are, therefore, expected to satisfy these antisymmetries better for higher temperatures where $P_{cr}(\varrho, T)$ is negligible and so $P_k(\varrho, T)$ actually approximates both $P_{cl}(\varrho, T)$ and $P(\varrho, T)$. In particular, we note that expression (15) implies that higher isothermal derivatives $\partial^i P/\partial \varrho^i$, $i = 6, 7, \ldots$, of real fluids cannot possibly have zeros in the vicinity of the critical density, which explains the observed stronger temperature dependence of approximations to these zeros in the vicinity of the critical temperature.

Now, according to Thom's theory of catastrophes it may not be incidental that the density line $\varrho = \varrho_{cc} \approx \varrho_c$ along which the fluids considered exibit approximately antisymmetries (10, 11, 12) passes near the critical point ϱ_c; on the contrary, occurrence of antisymmetries may be considered as indicating on the above-critical isotherms the possibility of the liquid-gas phase transition at lower temperatures. If so, one immediately wonders whether also the approximate antisymmetries (10, 11, 12, 13) exhibited by fluids considered in the vicinity of the density line $\varrho = \varrho_{ac} = (2.7 \pm 0.3)\,\varrho_c$ signify that under certain thermodynamic conditions fluids exhibit a phase transition into a mesophase of an intermediary order between crystal and fluid; cf.[13], for discussion of another possibility.

To sum up: this and the preceding two papers[3,4] have brought forward remarkable new physical properties of the Lennard-Jones and of some real fluids. A variety of different analytic approximations $P_k(\varrho, T)$ to their P, ϱ, T surfaces display approximate isothermal antisymmetries (6, 7, 8, 9), also on extrapolated isotherms far away from the regions of their approximate validity. These approximate antisymmetries manifest themselves analytically in the fact that on computing certain combinations of higher order isothermal derivatives $\partial^i P_k/\partial \varrho^i$ for various approximations $P_k(\varrho, T)$ pertaining to the same fluid, we notice many of them exhibiting slightly temperature dependent zeros in the vicinity of density ϱ_c of the liquid — gas phase transition and within the density interval $[2.4\,\varrho_c, 3\,\varrho_c]$, though their numerical values may differ in sign as well as in magnitude up to a few orders, as various approximations to higher derivatives are expected to.

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LOKALNE ANTISIMETRIJE IZOTERMNEGA OBNAŠANJA LENNARD-JONESOVE IN REALNIH TEKOČIN

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Analizirajoč nadkritično izotermno obnašanje mnogih eksperimentalno določenih enačb stanja različnih tekočin smo prišli do rezultatov, ki nakazujejo da je $\partial^4 P/\partial \varrho^4$ močno antisimetričen v okolici kritične gostote ϱ_c in v okolici 2.7 ϱ_c, ter da je drugi izotermni odvod kemičnega potenciala antisimetričen v okolici 2.7 ϱ_c.