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THE EQUATION OF STATE FOR DENSE LIQUID MIXTURES OBTAINED BY AN INTEGRAL EQUATION METHOD

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[1] **Paper presented at the Thirteents Simposium on Thermophysical Properties, June 22-27, 1977, Boulder, Colorado, U.S.A.**

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ABSTRACT

The equation of state for liquid mixtures is fundamental problem of the statistical theory. This problem can be solved by the approximation of the pair additivity of the intermolecular potential $\varphi_{\alpha\beta}(r)$ by the method of integral equations for binary distribution functions $g_{\alpha\beta}(r)$.

This approach allowed to determine satisfactory the thermophysical properties both model and real liquid systems only if their densities are small or moderate. For dense liquid mixtures, new integral equations have be deduced. For this purpose, the Lebowitz-Percus method is applied as a rule. In this method the chosen generation functional (GF) is expanded in series with respect to deviation of the local density from its average value. Choice of the GF is obtained a priori .

In this report, the physical principle for the choice GF is given. It is shown that the scaled transformation of the coordinate part of phase space of one component of the mixture corresponds to virtual variation of the local density of this component. This result was applied to develop the procedures of the forming GF, which can be used in the system integral equations for $g_{\alpha\beta}(r)$. On basis of developed theory, the equation of state for dense liquid mixtures was obtained. This equation of state is modification of known equations proposed by Tait and Marnaghan. It was also shown that system of integral equations for $g_{\alpha\beta}(r)$ coincide with Percus-Yevick system of equations or hypernetted chains equations system.

KEY WORDS: activity; equation of state; generation functional; liquid; mixture; pressure.

1. INTRODUCTION

In the last time scientists take much attention to investigation of different equilibrium properties of liquid mixtures by a methods of integral equations.

In article [1] it was presented such the system of integral equations. If integral equations for conditional distribution functions are deduced, usual it was used the Lebowitz-Percus method [2]. This method is based on the Taylor-series expansion of the GF $\Phi\left[F_1^{\alpha}(\vec{r}|\psi_\alpha), \psi_\alpha(\vec{r})\right]$ with respect to variations in position of the particle, which creats the field $\psi_\alpha(\vec{r})$. GF $\Phi\left[F_1^{\alpha}(\vec{r}|\psi_\alpha), \psi_\alpha(\vec{r})\right]$ depends on external field $\psi_\alpha(\vec{r})$ and first order conditional distribution function $F_1^{\alpha}(\vec{r}|\psi_\alpha)$ for α-component of a mixture.

Unfortunately, the physical principle is absent for selection of the GF. Usually it is selected a priori intuitively, as this was performed in Percus-Yevick (PY) or in hypernetted-chain (HNC) approximation. In addition if GF is selected, it is impossible to indicate the criterion of the applicability of the obtained integral equations for radial distribution functions (RDF) $g_{\alpha\beta}(r)$. These difficulties are associated with unknown character of the $F_1^{\alpha}(\vec{r}|\psi_\alpha)$ from $\psi_\alpha(\vec{r})$. That is why it is necessary to find simple approximation of the $\psi_\alpha(\vec{r})$ dependence from density $\rho_\alpha = N_\alpha/V$, where α is one from components of a mixture, N_α is total number of the α-type particles and V is mixture volume.

2. THE METHOD OF THE LOCAL SCALED TRANSFORMATION OF PHASE SPACE

We used the method of the local scaled transformation of the coordinate spase of the α- mixture component. In accordance with [3,4] it is felt that scaled transformation with scaled factor

$$\chi_\alpha(\vec{r}) = \left(\frac{V\alpha}{V_0}\right)^{1/3} = \left(\frac{\rho_0^\alpha}{\rho_\alpha}\right)^{1/3}, \qquad (1)$$

which is depended from the space argument $\vec{r}$, corresponds to virtual variation of the density of the α-component, that is $\rho_0^\alpha(\vec{r}) \to \rho_\alpha(\vec{r})$. V_0 and ρ_0^α in (1) are the volume and density of the reference state; V_α, ρ_α-are analogical values of our system after of the α-type particle coordinates of the scaled transformation.

Really, after such transformation the coordinate $\vec{r}_i^{\,\alpha}$ and the first order distribution function $F_1^\alpha(\vec{r}_1^{\,\alpha})$ which is determined in large canonical ensemble as

$$F_1^\alpha(\vec{r}_1^{\,\alpha}) = \frac{E_1^\alpha}{E} = \frac{1}{E}\sum_{N_1\geq 0}\cdots\sum_{N_\alpha\geq 1}\cdots\sum_{N_n\geq 1}\frac{Z_\alpha^{N_\alpha}}{(N_\alpha-1)!}\prod_{k\neq\alpha}\frac{Z_k^{N_k}}{N_k\,!}\int D_N d\vec{r}_2^{\,\alpha}\cdots d\vec{r}_{N_\alpha}^{\,\alpha}\prod_{k\neq\alpha}\left\{d\vec{r}_{N_\alpha}^{\,\alpha}\right\} \qquad (2)$$

***w*ill become equal**

$$\vec{r}_i^{\,\alpha} \to \chi_\alpha(\vec{r}_i^{\,\alpha})\vec{r}_i^{\,\alpha} = \vec{r}_i^{\,\alpha} + k_\alpha(\vec{r}_i^{\,\alpha})\vec{r}_i^{\,\alpha}$$

and

$$F_1^\alpha\left[\chi_\alpha(\vec{r}_i^{\,\alpha})\vec{r}_i^{\,\alpha}\right] = F_1^\alpha(\vec{r}_i^{\,\alpha}) + a_1^\alpha(\vec{r}_i^{\,\alpha}) - F_1^\alpha(\vec{r}_1^{\,\alpha})a_2^\alpha + 0([k_\alpha(\vec{r}_1^{\,\alpha})]^2), \qquad (3)$$

where E is statistical sum

$$E = \sum_{N_1\geq 0}\cdots\sum_{N_n}\prod_{k=1}^{n}\frac{Z_k^{N_k}}{N_k\,!}\int D_N\prod_{k=1}^{n}\left\{d\vec{r}_{N_k}^{\,k}\right\}, \qquad (4)$$

$Z_k = \exp(\mu_k / k_B T)$**– is activity, μ_k-is chemical potential of the k-mixture component, ($N_1+N_2+...+N_n=N$),** $D_N(\vec{r}_1,\cdots,\vec{r}_N) = \exp(-U_N / k_B T)$, $U_N(\vec{r}_1,\cdots,\vec{r}_N) = (1/2)\sum_{\alpha,\beta}\sum_{i<j}\varphi_{\alpha_i\beta_j}(r_{ij})$ **-is potential energy,** $\varphi_{\alpha_i\beta_j}$ **-is pair potential energy,** $\left\{d\vec{r}_{N_k}^{\,k}\right\} = \prod_{i=1}^{N_k} d\vec{r}_i^{\,k}$**, n is number of a mixture components. In formula (3)** a_i^α **are the following**

$$a_1^\alpha = 3\int F_2^{\alpha\alpha}(\vec{r}_1^{\,\alpha},\vec{r}_2^{\,\alpha})k_\alpha(\vec{r}_2^{\,\alpha})d\vec{r}_2^{\,\alpha} - \frac{1}{k_B TE}\sum_{N_1\geq 0}\cdots\sum_{N_\alpha\geq 1}\cdots\sum_{N_n\geq 0}\frac{Z_\alpha^{N_\alpha}}{(N_\alpha-1)!}\times\uparrow$$

$$\prod_{k\neq\alpha}\frac{Z_k^{N_k}}{N_k!}\int\sum_{i=1}^{N_\alpha}D_n\nabla_{\vec{r}_i^{\,\alpha}}U_N k_\alpha(\vec{r}_i^{\,\alpha})\vec{r}_i^{\,\alpha}\prod_{i=2}^{N_\alpha}\left\{d\vec{r}_i^{\,\alpha}\right\}\prod_{k\neq\alpha}\left\{d\vec{r}_{N_k}^{k}\right\} \quad , \qquad \textbf{(5)}$$

$$a_2^\alpha = 3\int F_1^\alpha(\vec{r}_2^{\,\alpha})k_\alpha(\vec{r}_2^{\,\alpha})d\vec{r}_2^{\,\alpha} - \frac{1}{k_B T}\sum_{N_1\geq 0}\cdots\sum_{N_n}\prod_{k=1}^{n}\frac{Z_k^{N_k}}{N_k!}\int\sum_{i=1}^{N_\alpha}D_N\times$$

$$\nabla_{\vec{r}_i^{\,\alpha}}U_N k_\alpha(\vec{r}_i^{\,\alpha})\prod_{i=1}^{N_\alpha}\left\{d\vec{r}_i^{\,\alpha}\right\}\prod_{k\neq\alpha}\left\{d\vec{r}_{N_k}^{k}\right\} \quad , \qquad \textbf{(6)}$$

$F_2^{\alpha\alpha}(\vec{r}_1^{\,\alpha},\vec{r}_2^{\,\alpha})$**- is pair distribution function. It cannot be too highly stressed that the expression (3) is deduced in approximation about smooth non-homogeneity with rejection of the terms containing** $\nabla k_\alpha(\vec{r}_i^{\,\alpha})$**. According to [5]**

$$\rho_\alpha\int\left[F_2^{\alpha\alpha}(\vec{r}_1^{\,\alpha},\vec{r}_2^{\,\alpha}) - F_1^\alpha(\vec{r}_1^{\,\alpha})F_1^\alpha(\vec{r}_2^{\,\alpha})\right]d\vec{r}_1^{\,\alpha}d\vec{r}_2^{\,\alpha} = \frac{k_B T}{\rho_\alpha}\left(\frac{\partial\rho_\alpha}{\partial\mu_\alpha}\right)_{T,\mu_k,V} - 1 \qquad \textbf{(7)}$$

and by theorem of virial for pressure P

$$P = k_B\rho T - \frac{1}{6}\sum_{\alpha,\beta}\rho_\alpha\rho_\beta\int\vec{r}\vec{\nabla}\varphi_{\alpha\beta}(\vec{r})g_{\alpha\beta}(\vec{r})d\vec{r} \qquad \textbf{(8)}$$

we deduced for $F_1^\alpha[\chi_\alpha(\vec{r}_1^{\,\alpha})\vec{r}_1^{\,\alpha}]$

$$F_1^\alpha\left[\chi_\alpha(\vec{r}_1^{\,\alpha})\vec{r}_1^{\,\alpha}\right] = F_1^\alpha(\vec{r}_1^{\,\alpha}) - 3k_\alpha(\vec{r}_1^{\,\alpha})F_1^\alpha(\vec{r}_1^{\,\alpha})\left[1 - \frac{k_B T}{\rho_\alpha}\left(\frac{\partial\rho_\alpha}{\partial\mu_\alpha}\right)_{T,\mu_k,V} + \frac{6}{k_B T}(P_1^\alpha - P_\alpha)k_\alpha\right] \qquad \textbf{(9)}$$

where P_α**-is partial pressure of the** α**-component,** P_1^α**- is partial pressure of the** α**-component in the external field, which is created by additional particle of the** α**-component in point** $\vec{r}_1^{\,\alpha}$ **.**

It was shown [6] that for system with pair-additional intermolcular energy $P_\alpha \cong P_1^\alpha$**. Since for dense liquid mixtures and condensed gases far from stability boundary the partial susceptibility is much letter than 1, that is** $k_B T(\partial\rho_\alpha / \partial\mu_\alpha)_{T,\mu_k,V} / \rho_\alpha << 1$ **, the expression (9) are rewritten as**

$$F_1^{\alpha}(\vec{r}_1^{\alpha}) / F_1^{\alpha}[(\chi_{\alpha}(\vec{r}_1^{\alpha})\vec{r}_1^{\alpha}] = [\chi_{\alpha}(\vec{r}_1^{\alpha})]^3 \ . \qquad (10)$$

Therefore it is thought, that the scaled transformation of the coordinate space of α- mixture component with scaled factor $\chi_{\alpha}(\vec{r}_i^{\alpha})$ corresponds to the virtual variation of the local density of the α-component.

3. CHOICE OF THE GENERATING FUNCTIONAL

We want to deduce the system of integral equations for RDF of a liquid mixtures.

Let us consider the possibility of use above mentioned conclusion for choice of the GF. According to [7] the GF is analitical function from $u = \psi_{\alpha}(\vec{r}) / k_B T$ **and** $\upsilon = F_1^{\alpha}(\vec{r}|\psi_{\alpha}) - F_1^{\alpha}(\vec{r}|0)$, **that is**

$$\Phi[u, \upsilon] = \sum_{i,j} a_{ij} u^i \upsilon^j \qquad (11)$$

where a_{ij} are constants. If we the consider only the special case when compressibility is small and

$$\Phi[u, \upsilon] = a_{00} + a_{10} u + a_{01} \upsilon \ ,$$

and we decompose of it in Taylor-series expansion with respect to deviations $F_1^{\alpha}(\vec{r}|\psi_{\alpha}) - F_1^{\alpha}(\vec{r}|0)$, **we deduce**

$$\Phi\left[\frac{1}{k_B T}\psi_{\alpha}(\vec{r}), F_1^{\alpha}(\vec{r}|\psi_{\alpha}) - F_1^{\alpha}(r|0)\right] = a_{00} + a_{01}(F_1^{\alpha}(\vec{r}|\psi_{\alpha} - F_1^{\alpha}(\vec{r}|0)) +$$

$$a_{10}\sum_{\gamma} \frac{\delta(\psi_{\alpha}(\vec{r}) / k_B T)}{\delta F_1^{\gamma}(\vec{r}'|\psi_{\gamma})}\Big|_{\psi=0} [F_1^{\gamma}(\vec{r}'|\psi_{\gamma}) - F_1^{\gamma}(\vec{r}'|0)] d\vec{r}' \qquad (12)$$

In (12), the terms which contain high order derivative from $\psi_{\alpha}(\vec{r})$, are ignored. This implies that we ignore the multiparticle correlations, which are essential near critical point.

If we use the functional determination of the direct correlative function (DCF) $C_{\alpha\beta}(r)$ and system of Ornstein-Zernice (OZ) equations, then we deduce next expression for DCF from (12)

$$a_{10}C_{\alpha\beta}(|\vec{r}-\vec{r}'|) = a_{00} + a_{10}[g_{\alpha\beta}(|\vec{r}-\vec{r}'|) - 1] - \Phi(\varphi_{\alpha\beta}(|\vec{r}-\vec{r}'|)/k_BT, g_{\alpha\beta}(|\vec{r}-\vec{r}'|) - 1) \quad (13)$$

The next conclusion follows immediately from (13), that choice of GF $\Phi[u,\upsilon]$ is equivalent to choice of the DCF.

So far as we differentiate the $\Phi[u,\upsilon]$ in point $\psi(\vec{r}) = 0$, $\Phi[u,\upsilon]$(11) may be rewrite as

$$\Phi[u,\upsilon] = \upsilon\sum_{i=1}^{\infty} a_{i1}u^i. \quad (14)$$

To take into account the next terms of expansion (12), we use Kummer transformation [8], according to which

$$\upsilon\sum_i a_{i1}u^i = A + \upsilon\sum_i a_{i1}(u^i - u_0^i) \quad (15)$$

where $A = \upsilon\sum_i a_{i1}u_0^i$ and u_0-is subsidiary function. It satisfies to next condition:

$$(u-u_0)/u_0 = 0(u_0) \quad (16)$$

In purturbation theory, any model potential is considered as function u_0. Nevertheless, we consider, as an alternative to function u_0, analogous potential which was scaled transformed. It can not be too highly stressed that the condition (16) is true if scaled factor $\chi_\alpha(\vec{r})$ is close to 1, for smooth potential function. Because the expression $\upsilon\sum_i a_{i1}(u^i - u_0^i)$ converges more quickly than expression (14) if the condition (16) is satisfied, therefore we chose as the GF Φ the tail of the expression (15), which is quickly convergent. Therefore the GF we deduce in such form

$$\Phi[F_1^\alpha(\vec{r}|\psi_\alpha), \psi_\alpha(\vec{r})] = \sum_i \frac{1}{k_BT} a_{i1}\left[(\psi_\alpha(\chi_\alpha\vec{r}))^i - (\psi_\alpha(\vec{r}))^i\right]F_1^\alpha(\vec{r}|\psi_\alpha) \quad (17)$$

We shall indicate new two variant of the GF , which are a consequence of the our theory. By analogy to functionals which were used in the PY theory and in the HNC [7] we built the GF

$$\Phi_1[F_1^{\alpha}(\vec{r}|\psi_\alpha), \psi_\alpha(\vec{r})] = F_1^{\alpha}(\vec{r}|\psi_\alpha)\exp\{-[\psi_\alpha(\chi_\alpha\vec{r}) - \psi_\alpha(\vec{r})]/k_BT\}, \quad (18)$$

and

$$\Phi_2 = \ln\{\Phi_1[F_1^{\alpha}(\vec{r}|\psi_\alpha), \psi_\alpha(\vec{r})]\}. \quad (19)$$

If $\chi_\alpha \to \infty$, the GF (18) becomes similar to the PY ones, and GF (19) becomes similar to the HNC ones.

4. THE SYSTEM OF INTEGRAL EQUATIONS FOR RDF OF LIQUID MIXTURES

The system of the integral equations for RDF can result from the equation (17) by the Lebowitz-Percus method [2], if we take into account only linear terms this equation:

$$g_{\alpha\beta}(r)\hat{M}_{\vec{r}}(\chi_\alpha)\varphi_{\alpha\beta}(r) + \hat{M}_{\vec{r}}(\chi_\alpha)[g_{\alpha\beta}(r) - 1] - \sum_\gamma \rho_\gamma \int g_{\alpha\gamma}(|\vec{r} - \vec{r}'|)\times$$

$$\hat{M}_{\vec{r}-\vec{r}'}(\chi_\alpha)\frac{1}{k_BT}\varphi_{\alpha\gamma}(|\vec{r} - \vec{r}'|)[g_{\gamma\beta}(r') - 1]d\vec{r}' = 0. \quad (20)$$

From this system of equations (20) it follows that DCF has the form, which satisfies the equation (21)

$$\hat{M}_{\vec{r}}(\chi_\alpha)C_{\alpha\beta}(r) = -g_{\alpha\beta}(r)\hat{M}_{\vec{r}}(\chi_\alpha)[\varphi_{\alpha\beta}(r)/k_BT] \quad (21)$$

with operator

$$\hat{M}_{\vec{r}}(\chi_\alpha) = \exp\{(\chi_\alpha - 1)\vec{r}\vec{\nabla}_{\vec{r}}\} - 1. \quad (22)$$

Next systems of the integral equations for RDF $g_{\alpha\beta}(r)$ can be deduced by method of functional differentiation of the GF (18) and (19)

$$g_{\alpha\beta}(r)\exp\{-[\varphi_{\alpha\beta}(\chi_\alpha r) - \varphi_{\alpha\beta}(r)]/k_BT\} = g_{\alpha\beta}(\chi_\alpha r) -$$

$$\sum_\gamma \rho_\gamma \int d\vec{s}[\exp\{-[\varphi_{\alpha\gamma}(\chi_\alpha s) - \varphi_{\alpha\gamma}(s)]/k_BT\} - 1]g_{\alpha\gamma}(s)[g_{\gamma\beta}(|\vec{r} - \vec{s}|) - 1] \quad (23)$$

and

$$\ln g_{\alpha\beta}(r) = g_{\alpha\beta}(\chi_\alpha r) - 1 + [\varphi_{\alpha\beta}(\chi_\alpha r) - \varphi_{\alpha\beta}(r)]/k_BT + \quad (24)$$

$$\sum_\gamma \rho_\gamma \int d\vec{s}\{g_{\alpha\gamma}(s) - 1 - \ln g_{\alpha\gamma}(s) + [\varphi_{\alpha\gamma}(\chi_\alpha s) - \varphi_{\alpha\gamma}(s)]/k_BT\}[g_{\gamma\beta}(|\vec{r} - \vec{r}'|) - 1]$$

if the DCF has form

$$C_{\alpha\beta}(r) - C_{\alpha\beta}(\chi_\alpha r) = g_{\alpha\beta}(r)[1 - \exp\{-[\varphi_{\alpha\beta}(\chi_\alpha r) - \varphi(r)]/k_BT\} \quad (25)$$

and

$$C_{\alpha\beta}(r) - C_{\alpha\beta}(\chi_\alpha r) = g_{\alpha\beta}(r) - 1 - \ln g_{\alpha\beta}(r) + [\varphi_{\alpha\beta}(\chi_\alpha r) - \varphi_{\alpha\beta}(r)] / k_B T \quad (26)$$

consequently.

The system of the integral equations (23) and (24) are transformed in PY and HNC systems if $\chi_\alpha \to \infty$ and $\rho_\alpha \to 0$, lim $\varphi_{\alpha\beta}(\chi_\alpha r)=0$, lim$C_{\alpha\beta}(\chi_\alpha r)=0$, consequently. In addition, the system of integral equations (23) is transformed in the (20) ones if $\chi_\alpha \to 0$ and temperature is high.

5. THE EQUATION OF STATE FOR LIQUID MIXTURES

The equation of state for dense liquid mixtures can be obtained from equations (20) with DCF (21), if $\chi_\alpha \to 0$ and differential operator $\hat{M}_{\vec{r}}$ (22) has form

$$\hat{M}_{\vec{r}}(0) = \exp(-\vec{r}\vec{\nabla}_{\vec{r}}) - 1 = \sum_{i=1}^{\infty} (-1)^i \frac{(\vec{r}\vec{\nabla}_{\vec{r}})^i}{i!} \quad . \quad (27)$$

And also we use the theorem of compressibility (28)

$$\frac{1}{k_B T}\left(\frac{\partial P}{\partial \rho_\alpha}\right)_{T,\rho_\beta} = 1 - \sum_\beta \rho_\beta \int C_{\alpha\beta}(r) d\vec{r} \quad (28)$$

and the virial theorem (8).

Let us consider the equation of state, which can be obtained if we are limited in expression (27) only by some N first terms:

1. N=1 $\quad \hat{M}_{\vec{r}} = -\vec{r}\vec{\nabla}_{\vec{r}}$.

Then expression (21) can be rewritten as

$$\vec{r}\vec{\nabla}_{\vec{r}} C_{\alpha\beta}(r) = -g_{\alpha\beta}(r)(\vec{r}\vec{\nabla}_{\vec{r}})\varphi_{\alpha\beta}(r) / k_B T . \quad (29)$$

Integrating the equation (29) on volume V and neglecting by the surface terms we obtain

$$3\int C_{\alpha\beta}(r) d\vec{r} = \frac{1}{k_B T}\int g_{\alpha\beta}(r)(\vec{r}\vec{\nabla}_{\vec{r}})\varphi_{\alpha\beta}(r) d\vec{r} \quad . \quad (30)$$

If we substitude the expression (30) in the theorem of virial (8) we obtain the equation of state in form

$$\rho\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{(P - k_B T\rho / 2)}{1/2} \quad . \quad (31)$$

This equation of state is similar to Marnaghan equation (32)

$$\rho\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{P+B}{A}, \qquad (32)$$

where parameteres B and A are equal

$$B=-\rho k_B T/2, \quad A=1/2.$$

In equation (32) parameter A is constant and parameter B is function from the temperature and the concentration. The results of the P-V-T date experimental investigations of liquid n-hexane+n-dodecane mixtures [10] agree closely with the equation (32), moreover it was shown that A is equal to 0.16÷0.09 and B is decreasing function from the temperature.

$$N=2 \qquad \hat{M}_{\vec{r}} = (\vec{r}\vec{\nabla}_{\vec{r}})^2/2 - \vec{r}\vec{\nabla}_{\vec{r}}\ .$$

If repulsing potential of the intetmolecular interaction is characterized by index m, that is $\varphi_{\alpha\beta}(r) \sim r^m$, then equation of state takes the form (32) with parameter $A= 3/(m+3)$ and $B=(A-1)\rho k_B T$. If $m \le 30$ the theoretical value of parameter A agree closely with its experimental value.

If N is arbitrary value in expression (27), for parameter A^{-1} we obtain:

$$A^{-1} = 12\left[\sum_{i=1}^{N}\frac{(m+i-1)!}{i!\,m!} \Big/ \sum_{i=1}^{N}\frac{(i+2)!}{i!}\right] \qquad (34)$$

and parameter B retains the form (33).

If index of repulsion is different for molecule of the type α and ,β, then equation of state takes the form (35)

$$P = \rho k_B T - \sum_{\alpha}\rho_\alpha \frac{3k_B T}{3+m_{\alpha\alpha}} + \sum_{\alpha,\beta}\rho_\alpha\rho_\beta \frac{3k_B T}{3+m_{\alpha\beta}}\left(\frac{\partial \mu_\beta}{\partial \rho_\alpha}\right)_{T,\rho_{\alpha\neq\beta}}. \qquad (35)$$

If inequality (36)

$$\left|m_{\alpha\beta} - m_{\gamma\lambda}\right| / m_{\alpha\beta} << 1 \qquad \{\alpha;\beta\} \neq \{\gamma;\lambda\} \qquad (36)$$

takes place, then equation of state takes the form (37)

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{P+B+\sum_{\alpha\beta} M_{\alpha\beta}}{A}, \qquad (37)$$

where

$$M_{\alpha\beta} = \frac{3}{(3+m)^2}\left[k_B T \rho_\alpha (m_{\alpha\beta} - m)\delta_{\alpha\beta} + \rho_\alpha \rho_\beta (m_{\alpha\beta} - m)\left(\frac{\partial \mu_\beta}{\partial \rho_\alpha}\right)_{T,\, \rho_{\alpha \neq \beta}}\right],$$

where $\delta_{\alpha\beta}$-is the symbol of Kronecker, m-index of repulsing potential of reference system.

CONCLUSION

Assuming that isothermal compressibility is small for liquid mixtures it is found the simple approximate relation, deseribing the change of the intermolecular potential with variation of the local density of α-component.

If isothermal compressibility is large for liquid mixtures, obtained system of integral equations for RDF is transformed in PY and HNC equations.

The equation of state, obtained on the basis of the developed theory has a functional form which is similar to the Marnaghan equation of state, if the index m of the repulsing intermolecular potential is common for molecules of α and β type. In opposite case, the equation of state is more complicated.

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