

FIRST ORDER PERTURBATION EXPANSION FOR SYSTEMS OF CONVEX MOLECULES

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A first order perturbation expansion is proposed for systems of convex molecules interacting *via* a pair potential of Kihara-core type; the perturbation term is given by a simple integral over the shortest distance between surfaces of two hard convex bodies corresponding to a pair of interacting molecules. For a special case of a square-well-core potential and with the use of the average pair correlation function at contact point, expressions were derived for thermodynamic functions of pure substances and mixtures and further employed for determining excess thermodynamic functions in carbon disulphide-tetrachloromethane, cyclopentane-tetrachloromethane and tetrachloromethane-benzene systems at 298.15 K.

In an earlier work^{1,2}, a statistical-thermodynamic description of systems containing nonspherical convex molecules has been proposed which makes it possible in the case of the pairwise additive potential energy of the studied system to express thermodynamic quantities as functions of three angles and the shortest distance between surfaces of two interacting molecules. By employing the scaled particle theory, approximate expressions have been found for the average pair correlation function at contact point and the equation of state as functions of geometric functionals of hard convex bodies — volume, surface and the integral of mean curvature.

This statistical-thermodynamic description has been applied in this work for formulating the perturbation expansion for systems of non-spherical nonpolar molecules; the system of hard convex bodies was taken as the reference system. Explicit relations for calculating thermodynamic functions of pure substances and mixtures have been derived for a square-well-core potential with a very narrow well; the use of this potential is due to the fact that the average correlation function is known only at the contact point.

THEORETICAL

The configuration integral of a one-component system containing N nonspherical molecules in volume V and at temperature T is given by the expression

$$Q(T, V, N) = \int \dots \int \exp[-\beta U_N] dq_1 dq_2 \dots dq_N, \quad (1)$$

where $\beta = (kT)^{-1}$, k is Boltzmann's constant and \mathbf{q}_i five- or six-dimensional vector³ given by the radius vector of the centre of gravity \mathbf{r}_i and by the orientation angles ω_i ;

$$d\mathbf{q}_i = d\mathbf{r}_i d\omega_i, \quad (2)$$

simultaneously

$$\int d\omega_i = 1. \quad (3)$$

If the potential energy U_N of the studied system may be expressed as the sum of the reference system potential energy U_N^0 and a perturbation W_N , the Helmholtz function F can be written as a perturbation expansion formally identical with Zwanzig's expression⁴

$$\beta(F - F^0) = -\ln(Q/Q^0) = \beta\langle W_N \rangle_0 - \frac{1}{2}\beta^2[\langle W_N^2 \rangle_0 - \langle W_N \rangle_0^2] + \dots \quad (4)$$

Index ⁰ denotes functions of the reference system and symbol $\langle \rangle_0$ a quantity averaged over different configurations of the reference system. The perturbation potential energy W_N may be expressed as a sum of pair interactions (plus substantially lower triplet terms *etc.*),

$$W_N = \sum_{i < j} w(\mathbf{q}_i, \mathbf{q}_j) + \dots \quad (5)$$

and the first order perturbation term can be then written in the following form

$$\beta\langle W_N \rangle_0 = \frac{1}{2}\beta \int w(\mathbf{q}_1, \mathbf{q}_2) n^0(\mathbf{q}_1, \mathbf{q}_2) d\mathbf{q}_1 d\mathbf{q}_2 = \frac{1}{2}\beta n^2 \int w(\mathbf{q}_1, \mathbf{q}_2) g^0(\mathbf{q}_1, \mathbf{q}_2) d\mathbf{q}_1 d\mathbf{q}_2. \quad (6)$$

In Eq. (6), n is the number density, $n^0(\mathbf{q}_1, \mathbf{q}_2)$ and $g^0(\mathbf{q}_1, \mathbf{q}_2)$ the generic distribution, resp. correlation function and $w(\mathbf{q}_1, \mathbf{q}_2)$ an intermolecular interaction potential of a pair of molecules with their mass centres at \mathbf{r}_1 and \mathbf{r}_2 and orientations ω_1 and ω_2 .

In view of the fact that the pair potential depends only on the mutual position and orientation of interacting particles, expression (6) may be simplified by transforming variables from $(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2)$ to $(\mathbf{r}_1, \omega_1, \mathbf{r}_{12}, \omega_{12})$ and by following integration over \mathbf{r}_1 and ω_1 as the pair potential does not depend on these two variables. By performing these operation, Eq. (7) results

$$\beta(F - F^0) = \frac{1}{2}\beta N n \int w(\varrho) g^0(\mathbf{r}_{12}, \omega_{12}) d\mathbf{r}_{12} d\omega_{12}. \quad (7)$$

From the metrics of convex bodies (*e.g.* Kihara⁵), vector \mathbf{r}_{12} may be expressed with the help of angles Θ and φ and distance ϱ (Fig. 1),

$$\mathbf{r}_{12} = \mathbf{r}_1(\Theta, \varphi) + \mathbf{r}_2(\Theta, \varphi) + \varrho \mathbf{u}(\Theta, \varphi), \quad (8)$$

where \mathbf{u} is the unit vector of the supporting (tangential) plane at contact with body **1**, resp. **2**, and determined by angles Θ and φ ; ϱ is the shortest distance between surfaces of the two bodies and $\mathbf{r}_1, \mathbf{r}_2$ radius vectors pointing from origin \mathbf{O}_1 at the contact point, resp. from the contact point at origin \mathbf{O}_2 .

For a given mutual orientation of both molecules given by ω_{12} (for simplicity we denote further $\omega = \omega_{12}$), it holds

$$d\mathbf{r}_{12} = \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_{12}}{\partial \Theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right) d\Theta d\varphi d\varrho, \quad (9)$$

so that

$$\beta(F - F^0)/N = \frac{1}{2} \beta n \iiint \iiint w(\varrho) g^0(\varrho, \Theta, \varphi, \omega) \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_{12}}{\partial \Theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right) d\Theta d\varphi d\omega d\varrho. \quad (10)$$

By introducing the average correlation function $g_{\text{av}}^0(\varrho)$ with the help of the relation

$$\begin{aligned} & \iiint \iiint g^0(\varrho, \Theta, \varphi, \omega) \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_{12}}{\partial \Theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right) d\Theta d\varphi d\omega = \\ & = g_{\text{av}}^0(\varrho) \iiint \iiint \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_{12}}{\partial \Theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right) d\Theta d\varphi d\omega = g_{\text{av}}^0(\varrho) S_{\mathbf{e}+\mathbf{e}+\mathbf{e}}, \end{aligned} \quad (11)$$

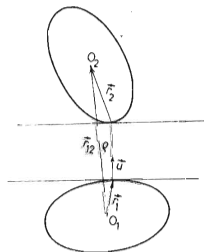


FIG. 1

Geometry of Convex Bodies with Their Surfaces Separated by a Distance ϱ

(where S_{c+q+c} is the surface resulting from the motion of the centre of particle 2 at a constant distance q between surfaces of the two particles, and averaged over all mutual orientations of both particles), it is possible in the first order perturbation term to go over into the integral over the variable distance q ,

$$\beta(F - F^0)/N = \frac{1}{2}\beta n \int_0^\infty w(q) g_{av.}^0(q) S_{c+q+c} dq. \quad (12)$$

For a mixture of several types of molecules (i, j etc.) at a composition given by mole fractions x_i , a relation similar to Eq. (12) holds,

$$\beta(F_s - F_s^0)/N = \frac{1}{2}\beta n \sum_{i,j} x_i x_j \int_0^\infty w_{ij}(q) (g_{av.}^0)_{ij}(q) S_{i+q+j} dq. \quad (13)$$

F_s and F_s^0 denote the free energy of the studied and reference mixture, w_{ij} and $(g_{av.}^0)_{ij}$ the interaction potential and the average correlation function of a pair of molecules i and j and S_{i+q+j} is the average surface of a pair of convex particles corresponding to molecules i and j and separated by distance q .

Perturbation Expansion for the Square-Well-Core Potential with Narrow Well

As contemporarily only values of the function $(g_{av.}^0)_{ij}$ at contact are known, we limit our further considerations to the case of the square-well-core potential given by Eq. (14)

$$\begin{aligned} w_{ij}(q) &= \infty, & \text{for } q \leq 0, \\ w_{ij}(q) &= -\varepsilon_{ij}, & \text{for } 0 < q \leq \Delta, \\ w_{ij}(q) &= 0, & \text{for } q > \Delta, \end{aligned} \quad (14)$$

where the distance Δ is so small that the particle density in the layer of the thickness Δ is constant. Then Eqs (12) and (13) may be written in the form of

$$\beta(F - F^0)/N = -\frac{1}{2}\beta n \varepsilon g_{av.}^0(0) S_{c+c} \Delta. \quad (15)$$

and

$$\beta(F_s - F_s^0)/N = -\frac{1}{2}\beta n \sum_{i,j} x_i x_j \varepsilon_{ij} (g_{av.}^0)_{ij}(0) S_{i+j} \Delta. \quad (16)$$

By introducing the symbol

$$\beta \varepsilon_{ij} \Delta = a_{ij}, \quad (17)$$

it is possible to obtain for the pure component i the expression

$$(F_i - F_i^0)/NkT = -\frac{1}{2}na_{ii}(g_{av}^0)_{ii}(0) S_{i+i} \quad (18)$$

and for the mixture

$$(F_s - F_s^0)/NkT = -\frac{1}{2}n \sum_{i,j} x_i x_j a_{ij}(g_{av}^0)_{ij}(0) S_{i+j}. \quad (19)$$

A simple relation holds between the average surface S_{i+j} and the geometric functionals of the hard convex bodies i and j

$$S_{i+j} = S_i + S_j + 8\pi R_i R_j, \quad (20)$$

where V_i , S_i , R_i denote the volume, surface and $(1/4\pi)$ -multiple of the integral of mean curvature of a convex body⁶ corresponding to a molecule i .

It has been shown in an earlier work¹ that the correlation function $g(0, \Theta, \varphi, \omega)$ at the contact point $\varrho = 0$ may be approximated by the relation

$$g^0(0, \Theta, \varphi, \omega) \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_{12}}{\partial \Theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right) = A \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_{12}}{\partial \Theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right) + \\ + \frac{1}{2} B \left[\mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_{12}}{\partial \Theta} \times \frac{\partial \mathbf{r}_2}{\partial \varphi} \right) + \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_2}{\partial \Theta} \times \frac{\partial \mathbf{r}_{12}}{\partial \varphi} \right) \right] + C \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_2}{\partial \Theta} \times \frac{\partial \mathbf{r}_2}{\partial \varphi} \right), \quad (21)$$

which leads to an equation of state for hard convex bodies in the form

$$\beta P^0/n = 1/(1-y) + 3\alpha y/(1-y)^2 + 3\alpha^2 y^2/(1-y)^3. \quad (22)$$

Quantities y and α are given by relations (23) and (24) as

$$y = nV_c \quad \text{and} \quad \alpha = R_c S_c / 3V_c; \quad (23), (24)$$

it then holds for coefficients A , B , C in Eq. (21)

$$A = 1/(1-y) + 3\alpha y/(1-y)^2 + 3\alpha^2 y^2/(1-y)^3, \quad (25)$$

$$B = -3\alpha y/(1-y)^2 - 6\alpha^2 y^2/(1-y)^3, \quad (26)$$

$$C = 3\alpha^2 y^2/(1-y)^3. \quad (27)$$

A relation for $(g_{av.}^0)_{ii}(0) S_{i+i}$ follows from Eq. (11)

$$(g_{av.}^0)_{ii}(0) S_{i+i} = A(2S_i + 8\pi R_i^2) + B(S_i + 4\pi R_i^2) + CS_i. \quad (28)$$

A relatively simple form for the first order perturbation expansion of the free energy results after substituting relation (28) into Eq. (18) and by using Eqs (25)–(27)

$$(F_i - F_i^0)/NkT = -\frac{1}{2}na_{ii}\{[2/(1 - y_i) + 3\alpha_i y_i/(1 - y_i)^2](S_i + 4\pi R_i^2) + [3\alpha_i^2 y_i^2/(1 - y_i)^3] S_i\}. \quad (29)$$

As on the right-hand side of Eq. (29) only the quantity a_{ii} depends on temperature, an equation holds for the internal energy U

$$(U_i - U_i^0)/NkT = (F_i - F_i^0)/NkT, \quad (30)$$

i.e.

$$(\bar{S}_i - \bar{S}_i^0)/Nk = 0. \quad (31)$$

By differentiating relation (29) with respect to the density, the perturbation expansion of the compressibility factor $z = \beta P/n$ results

$$z_i - z_i^0 = -n_i a_{ii}\{[1/(1 - y_i)^2 + 3\alpha_i y_i/(1 - y_i)^3](S_i + 4\pi R_i^2) + \frac{3}{2}[\alpha_i^2 y_i^2/(1 - y_i)^4] S_i\}. \quad (32)$$

The compressibility factor z_i^0 of the reference system is given by Eq. (22) from which the reference configuration Helmholtz function may be also determined

$$(F_i^0 - F_i^*)/NkT = -\ln(1 - y_i) + 3\alpha_i y_i/(1 - y_i) + \frac{3}{2}\alpha_i^2 y_i^2/(1 - y_i)^2; \quad (33)$$

F_i^* is the free energy of ideal gas at the given conditions.

Thermodynamic functions for the mixture may be determined similarly from values of average correlation functions at contact for individual component pairs. For an arbitrary $i - j$ pair in the solution, the correlation function is again approximated by relation (21), but coefficients A_{ij} , B_{ij} , C_{ij} are given by relations (34)–(36)

$$A_{ij} = \frac{1}{(1 - v)} + \frac{S_j(r - t) + T_j s}{(1 - v)^2} + \frac{S_j q s}{3(1 - v)^3}, \quad (34)$$

$$B_{ij} = -\frac{2S_j(r - t) + s(2T_j - R_i^2 S_j/S_i R_j)}{(1 - v)^2} - \frac{2S_j q s}{3(1 - v)^3}, \quad (35)$$

$$C_{ij} = \frac{S_j(r-t) + s(T_j - R_i^2 S_j / S_i R_j)}{(1-v)^2} + \frac{S_j q s}{3(1-v)^3} \quad (36)$$

The different symbols in Eqs (34)–(36) are defined as

$$T_k = 4\pi R_k^3 / S_k, \quad (37)$$

$$v = \sum_k n_k V_k, \quad s = \sum_k n_k S_k, \quad r = \sum_k n_k R_k, \quad (38), (39), (40)$$

$$q = \sum_k n_k R_k^2, \quad t = \sum_k n_k T_k, \quad n = \sum_k n_k. \quad (41), (42), (43)$$

It may be shown² that in this approximation of the correlation function the equation of state has the form

$$\beta P^0/n = 1/(1-v) + rs/n(1-v)^2 + qs^2/3n(1-v)^3. \quad (44)$$

By taking into account expressions (34)–(36) and the relation

$$(g_{sv}^0)_{ij}(0) S_{i+j} = A_{ij}(S_i + S_j + 8\pi R_i R_j) + B_{ij}(S_j + 4\pi R_i R_j) + C_{ij} S_j, \quad (45)$$

which follows from Eq. (11), functions $(F_s - F_s^0)/NkT = (U_s - U_s^0)/NkT$ may be determined from relation (19).

The perturbation expansion of the compressibility factor of the mixture can be obtained from this expression as

$$\begin{aligned} z_s - z_s^0 = & -\frac{1}{2} \sum_{i,j} x_i x_j a_{ij} \times \\ & \times \left\{ \left[\frac{1}{(1-v)^2} + \frac{2S_j(r-t) + 2T_j s}{(1-v)^3} + \frac{S_j q s}{(1-v)^4} \right] (S_i + S_j + 8\pi R_i R_j) + \right. \\ & + \left[-\frac{4S_j(r-t) + 2s(2T_j - R_i^2 S_j / R_j S_i)}{(1-v)^3} - \frac{2S_j q s}{(1-v)^4} \right] (S_j + 4\pi R_i R_j) + \\ & \left. + \left[\frac{2S_j(r-t) + 2s(T_j - R_i^2 S_j / R_j S_i)}{(1-v)^3} + \frac{S_j q s}{(1-v)^4} \right] S_j \right\}; \quad (46) \end{aligned}$$

z_s^0 is given by Eq. (44) which makes it also possible to calculate the configura-

tional free energy of a mixture of convex bodies of different types

$$(F_s^0 - F_s^*)/NkT = -\ln(1-v) + rs/n(1-v) + qs^2/6n(1-v)^2. \quad (47)$$

It is obvious that it holds for the entropy similarly as in the case of pure components

$$(\bar{S}_s - \bar{S}_s^0)/Nk = 0. \quad (48)$$

By combining Eqs (31), (33), (47) and (48), a relation for the excess entropy ΔS^E may be obtained as

$$T\Delta S^E = RT \sum_i x_i \left\{ \ln \frac{\bar{V}_s(1-v)}{\bar{V}_i(1-y_i)} + 3 \left[\frac{\alpha_i y_i}{(1-y_i)} - \frac{rs}{3n(1-v)} \right] + \frac{1}{2} \left[\frac{\alpha_i^2 y_i^2}{(1-y_i)^2} - \frac{qs^2}{9n(1-v)^2} \right] \right\}, \quad (49)$$

(where \bar{V}_s and \bar{V}_i are molar volumes of the mixture and pure component i , resp.). It may be shown that Eq. (18) in ref.⁷ is a special case of the last relation for spherical molecules, *i.e.* for $\alpha_i = 1$. Remaining excess functions follow by a combination of the perturbation expansions for the mixture and the pure component, with the possible use of Eq. (49).

COMPUTATIONS

The derived perturbation expansions were used for determining thermodynamic excess functions ΔV^E , $T\Delta S^E$, ΔH^E and ΔG^E of three binary mixtures at 25°C. For the calculations, the values of volumes, surfaces and $(1/4\pi)$ -multiples of the integrals of mean curvature of corresponding cores of convex bodies were used as found from correlations of heats of vaporization of pure components⁸. In the case of benzene, Kihara's values⁵ were employed; the thicknesses of parallel convex bodies were adjusted to yield experimental values of the entropy of vaporization at 25°C. The employed values of the geometric functionals of hard parallel bodies R_c , S_c , V_c are given in Table I together with values of the energetic parameter $a_{ii} = \varepsilon_{ii} \Delta/kT$ which was determined from experimental values of the cohesion energy of the given pure component by use of relations (29), (30) for experimental values of volumes of pure components at the given conditions; the values of the molar volumes⁹ are also given in Table I.

The rule

$$a_{ij} = (a_{ii} a_{jj})^{1/2} \quad (50)$$

was assumed to hold for the mixture. Of the different excess functions, first of all the excess volume was calculated. For given values of the geometric functionals and energetic parameters a_{ii} of pure components, the volumes of the pure substances and the mixture of a given composition were calculated at a pressure $P \rightarrow 0$; ΔV^E follows by combining these values. The mixture

volume, employed for the calculation of the remaining functions, was obtained by adding $\Delta V_{\text{theor.}}^E$ and $\sum x_i V_i^0$. The geometric functionals of the mixture were determined from Eqs (38)–(43) for this volume of the mixture and employed further for calculating the excess entropy, enthalpy and Gibbs function.

The outlined procedure was used for computing thermodynamic excess functions in carbon disulphide–tetrachloromethane, cyclopentane–tetrachloromethane and tetrachloromethane–benzene systems. Molecules of the individual components in these systems may be well approximated by convex bodies of different shapes — the core of CCl_4 is a tetrahedron formed by the Cl atoms, that of CS_2 is a rod connecting the sulphur atoms whereas the core of cyclopentane or benzene is a penta- or hexagon, respectively.

A comparison of calculated and experimental^{10–12} values of the excess functions in these systems at 25°C and for equimolecular mixtures is given in Table II.

DISCUSSION

The method of the calculation of the thermodynamic excess functions of a mixture outlined in the second part of this work represents a first application of the proposed perturbation expansion for systems of convex molecules. As so far no suitable “pseudoexperimental” data (*e.g.* from Monte-Carlo computations) for systems of nonspherical expressions are known, a direct comparison between theoretical expressions and experiment is inevitable. This comparison includes in itself not only the requirement of correctness of the employed statistical-thermodynamic procedure and plausibility of accepted assumptions, but also a good approximation of intermolecular interactions and finding of adequate values of characteristic parameters of the pair potential.

Taking into account the simplicity of the employed potential and the fact that the structure of the liquid has been described only by the value of the distribution function at contact, the overall agreement of theoretical and experimental values of the thermodynamic excess functions of the three studied systems may be considered as good.

TABLE I

Values of the Geometric Functionals of Convex Bodies, Energetic Parameter a_{ii} and Molar Volume

Substance	$R_c, \text{Å}$	$S_c, \text{Å}^2$	$V_c, \text{Å}^3$	$a_{ii}, \text{Å}$	$V_i, \text{cm}^3/\text{mol}$
CS_2	2.376	63.375	42.121	1.550	60.63
C_5H_{10}	2.718	89.392	74.363	1.500	94.71
CCl_4	2.845	94.387	78.552	1.472	97.10
C_6H_6	2.805	91.825	70.029	1.456	89.40

TABLE II

Comparison of Calculated and Experimental Excess Functions for Binary Carbon Disulphide–Tetrachloromethane, Cyclopentane–Tetrachloromethane and Tetrachloromethane–Benzene Systems at 25°C and the Mole Fraction $x = 0.5$

Property	CS ₂ –CCl ₄ ¹⁰		C ₅ H ₁₀ –CCl ₄ ¹⁰		CCl ₄ –C ₆ H ₆ ¹⁰	
	theor.	exptl. ¹⁰	theor.	exptl. ¹⁰	theor.	exptl. ¹⁰
ΔV^E , cm ³ /mol	0.075	0.32	-0.005	-0.04	-0.007	0.0
$T\Delta S^E$, J/mol	55	125	17	43	2	33
ΔG^E , J/mol	24	172	43	34	4	82
ΔH^E , J/mol	79	297	61	77	6	115

It follows from a detailed analysis that the theoretical ΔV^E values have a correct sign in all three cases and a corresponding order of magnitude, their absolute values are, however, lower than the experimental data. This fact is probably due to the way of determining the volume from energetic parameters a_{ij} (calculated from the cohesion energy). The agreement between theoretical and experimental values of the remaining excess functions may be denoted as excellent for the cyclopentane–tetrachloromethane system and as good for the carbon disulphide–tetrachloromethane system. The agreement is only qualitative for the tetrachloromethane–benzene system; it shows itself up, however, that the use of the value of $\Delta V^E = 0$ for the calculations of functions $T\Delta S^E$, ΔG^E , ΔH^E leads to a considerable improvement of description of the thermodynamic behaviour of the last system (the functions assume values of 5.0, 15.0, 9.7 J/mol for an equimolar mixture). If we moreover use values of the geometric functionals leading to a somewhat higher heat of evaporation (*i.e.* 34620 instead of an experimental value of 33880 J/mol), very good agreement may be obtained (*i.e.* 38.3, 60.0, 21.7 J/mol, resp.; Table II).

The method proposed in this work for systems of convex molecules may be compared with a similar method suitable for systems of spherical molecules^{7,13}. If the so far considerable uncertainty in approximating the studied molecules by convex models is taken into account, it may be stated that the employed perturbation method yields a good description of the equilibrium behaviour of mixtures of nonpolar nonspherical molecules; the results of this procedure compare well with results of methods developed for the special case of spherical particles. A relative simplicity of the derived relations is an advantage of this procedure which makes it also possible to describe the behaviour of a relatively wide group of mixtures of nonpolar substances. The present lack of knowledge of the course of the radial distribution function in the entire range of distance is a factor limiting the successful usage of the proposed perturbation expansion for the description of behaviour of pure components and mixtures in a wide range of temperatures and densities.

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