A FIRST-ORDER PERTURBATION EXPANSION FOR SOLUTIONS OF MOLECULES INTERACTING THROUGH THE TRIANGLE-WELL CONVEX-CORE POTENTIAL

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A first-order perturbation expansion of systems of particles interacting through the pair potential of the Kihara noncentral type was employed for determining the excess thermodynamic functions in binary solutions containing nonspherical nonpolar molecules. The dependence of the averaged correlation function of representative hard convex bodies on the distance between the surfaces of convex cores was approximated by a simple formula based on Monte-Carlo data; parameters in the triangle-well convex-core potential were found from the heat of vaporization, liquid density and from combination rules for cross-terms.

Earlier papers in this series[1-3] described the application of the perturbation expansion in systems containing convex components to the behaviour of mixtures of molecules interacting through a square-well core potential either with an extremely narrow or a finite width of the interaction range (well). Expressions for the thermodynamic functions become considerably simplified by using this potential, however, it is only a coarse approximation to the real shape of the curve representing the intermolecular forces, and energy parameters of the given interaction potential differ considerably from known values (for the simplest molecules).

As a further step in our systematic study of the behaviour of nonpolar,nonspherical molecules, we have in this work studied systems with a somewhat more complex and more realistic model of intermolecular interactions.

THEORETICAL

It is assumed in the theoretical approach employed here that the potential energy of the system is pairwise additive and that the pair potential depends only on the shortest distance between two cores ascribed to the individual molecules. These convex cores are characterized by three geometric functionals: volume V_i, surface S_i and the $(1/4\pi)$-multiple of the integral of mean curvature, R_i. If R_{ij}, S_{ij} and V_{ij} are mean geometric functionals of a body formed by the centre of core 2 when it is moving around core 1 keeping contact on the surface of 1, the following relations hold[4]:

$$R_{ij} = R_i + R_j \,, \tag{1}$$

$$S_{ij} = S_i + S_j + 8\pi R_i R_j \,, \tag{2}$$

$$V_{ij} = V_i + V_j + R_i S_j + R_j S_i \,. \tag{3}$$

The triangle-well convex core potential employed can be expressed analytically as:

$$\begin{aligned} w(\varrho) &= \infty & &\text{for} \quad \varrho < 0 \\ &= -\varepsilon_{ij}(1 - \varrho/\gamma R_{ij}) & &0 < \varrho < \gamma R_{ij} \\ &= 0 & &\varrho < \gamma R_{ij} \,; \end{aligned} \tag{4}$$

$w(\varrho)$ is the pair interaction potential, ϱ is the shortest distance between surfaces of the cores (which, for simplicity, include here also parallel convex bodies – *e.g.*, for a rod-like molecule the core is a spherocylinder), ε_{ij} is the value of energy in the minimum and γ characterizes the range of attractive forces.

The system of hard convex bodies, which would be identical with cores of molecules investigated, represents – similarly to other potentials with an infinitely steep repulsive branch – a natural choice for the reference system; the perturbation potential is then given by Eq. (4) for $\varrho > 0$. The Helmholtz free energy of the examined system, which contains N particles in volume V at temperature T and with the number density n, can be calculated[1] from the first-order perturbation expansion (for convex molecules),

$$F/NkT = F^0/NkT + (n/2kT) \int_0^\infty w^{\mathrm{p}}(\varrho)\, g^0(\varrho)\, S_{i+\varrho+i}\, \mathrm{d}\varrho \,; \tag{5}$$

similarly, for a mixture whose composition is given by the mole fraction x_i, it holds

$$F_s/NkT = F_s^0/NkT + (n/2kT) \sum x_i x_j \int_0^\infty w_{ij}^{p}(\varrho)\, g_{ij}^0(\varrho)\, S_{i+\varrho+j}\, \mathrm{d}\varrho; \tag{6}$$

$$S_{i+\varrho+j} = S_{ij} + 8\pi R_{ij}\varrho + 4\pi\varrho^2 \,. \tag{7}$$

In view of the type of the potential and the choice of the reference system, g^0 is independent of temperature, so that the internal energy is given by $(U - U^\circ)/NkT = (F - F^0)/NkT$; the compressibility factor is obtained by differentiation with respect to n.

The dependence of the averaged correlation function on the distance was approximated by the following expression for the total correlation function $h(\varrho) = g^0(\varrho) - 1$:

$$h_{ij}(\varrho) = A_{ij} + B_{ij}\frac{S_{ij} + 4\pi R_{ij}\varrho}{S_{ij} + 8\pi R_{ij}\varrho + 4\pi\varrho^2}\,, \quad \varrho < b_{ij} \tag{8}$$

$$h_{ij}(\varrho) = 0\,, \quad \varrho > b_{ij}$$

with

$$b_{ij} = R_{ij}/g^0(\varrho = 0) \tag{9}$$

and A_{ij}, B_{ij} are obtained from the condition of zero value of h_{ij} at point b_{ij} and from the value of $h_{ij}(0)$ at $\varrho = 0$.

After insertion from Eqs (*4*), (*7*) and (*8*), the Helmholtz free energy of the mixture can be expressed as

$$\begin{aligned}(F_s - F_s^0)/NkT &= \tfrac{1}{2}n\beta \textstyle\sum x_i x_j \displaystyle\int_0^{\gamma R_{ij}} w_{ij}(\varrho)\,[1 + h_{ij}(\varrho)]\,S_{i+\varrho+j}\,\mathrm{d}\varrho = \\ &= -\tfrac{1}{2}n \textstyle\sum x_i x_j(\varepsilon_{ij}/kT)\,R_{ij}\displaystyle\int_0^{\gamma}(1 - x/\gamma)\,[1 + h_{ij}(x)]\,\times \\ &\quad\times (S_{ij} + 8\pi R_{ij}^2 x + 4\pi R_{ij}^2 x^2)\,\mathrm{d}x\,,\end{aligned} \tag{10}$$

with $x = \varrho/R_{ij}$. Integration and a rearrangement yield the following expression for $(F_s - F_s^0)/NkT$ (and a similar one for the Helmholtz free energy of a pure substance)

$$\begin{aligned}(F_s - F_s^0)/NkT = {} & -\tfrac{1}{2}n \textstyle\sum x_i x_j(\varepsilon_{ij}/kT)\,[\tfrac{1}{2}S_{ij}R_{ij}\gamma + 4\pi R_{ij}^3(\gamma^2/3 + \gamma^3/12) + \\ & + S_{ij}R_{ij}\frac{6G_{ij}^3\gamma + 2G_{ij}^2(\gamma - 1) - G_{ij}(8\gamma + 1) + 3}{12\gamma G_{ij}^2(G_{ij} + 1)} + \\ & + 4\pi R_{ij}^3\frac{2G_{ij}^2\gamma - G_{ij}(2\gamma + 1) + 1}{12\gamma G_{ij}^3(G_{ij} + 1)}\Bigg]\,,\end{aligned} \tag{11}$$

with $G_{ij} = g_{ij}\,(\varrho = 0)$. The compressibility factor is then given by

$$\begin{aligned}(P_s - P_s^0)\,V_s/NkT = {} & -\tfrac{1}{2}n \textstyle\sum x_i x_j(\varepsilon_{ij}/kT)\Big\{[\tfrac{1}{2}S_{ij}R_{ij}\gamma + 4\pi R_{ij}^3(\gamma^2/3 + \gamma^3/12)] + \\ & + \Bigg[S_{ij}R_{ij}\frac{6G_{ij}^3\gamma + 2G_{ij}^2(\gamma - 1) - G_{ij}(8\gamma + 1) + 3}{12\gamma G_{ij}^2(G_{ij} + 1)} +\end{aligned}$$

$$+ 4\pi R_{ij}^3 \frac{2G_{ij}^2\gamma - G_{ij}(2\gamma + 1) + 1}{12\gamma G(G_{ij} + 1)}\Bigg] -$$

$$- \Bigg[S_{ij}R_{ij} \frac{2G_{ij}^3(2\gamma + 1) + 2G_{ij}^2(8\gamma + 1) + 8G_{ij}(\gamma - 1) - 6}{12\gamma G(G_{ij} + 1)^2} +$$

$$+ 4\pi R_{ij}^3 \frac{-4G_{ij}^3\gamma + G_{ij}^2(4\gamma + 3) + G_{ij}(4\gamma - 2) - 3}{12\gamma G_{ij}^4(G_{ij} + 1)^2}\Bigg] V_s \left(\frac{\partial G_{ij}}{\partial V_s}\right)\Bigg\} . \qquad (12)$$

The properties of the reference mixture of hard convex bodies were determined from the equation of state, which possesses the following form:

$$P_s^0/nkT = 1/(1 - v) + rs/n(1 - v)^2 + qs^2(3 - v)/9n(1 - v)^3 ; \qquad (13)$$

and, for the pure component, from the expression

$$P^0/nkT = 1/(1 - y) + 3\alpha y/(1 - y)^2 + \alpha^2 y^2(3 - y)/(1 - y)^3 . \qquad (14)$$

These equations of state correspond with the following values of the averaged correlation function at the contact point of an $i - j$ pair in the mixture and of an $i - i$ pair in the pure component;

$$G_{ij} = \frac{1}{(1 - v)} + \frac{(S_i T_j + S_j T_i)\, s + S_i S_j (r - t)}{(1 - v)^2\, S_{ij}} + \frac{2S_i S_j q s}{9(1 - v)^3\, S_{ij}} , \qquad (15)$$

and

$$G_{ii} = \frac{1}{(1 - y)} + \frac{3}{2}\frac{\alpha y}{(1 - y)^2} + \frac{\alpha^2 y^2}{(1 - y)^3\,(1 + 4\pi R^2/S)} . \qquad (16)$$

Here, $T_i = 4\pi R_i^3/S_i$, $Q_i = R_i^2$, $y = nV_i$, $\alpha = R_i S_i/3V_i$, and functionals r, s, q, t and v (which replace in the expressions for the mixture the terms nR_i, nS_i and $y = nV_i$) are given by the general formula $z = n \sum x_i Z_i$.

The knowledge of the equation of state of hard convex bodies makes it possible to determine all thermodynamic functions in the reference system whereas the first-order perturbation term is then obtained from known values of the averaged correlation functions.

RESULTS AND DISCUSSION

The statistical-thermodynamic description of the behaviour of systems obeying the triangle-well convex-core potential was used for determining the excess thermodynamic functions in binary solutions formed by nonpolar, nonspherical molecules.

The following systems were investigated: argon–nitrogen, nitrogen–oxygen, carbon monoxide–methane and nitrogen–methane. The selection of these solutions for testing the theoretical relations proposed was motivated by the fact that interactions in the corresponding molecular pairs can be described relatively accurately by the Berthelot combination rule[5]. The following cores were ascribed to the molecules: a sphere to argon, spherocylinders to nitrogen, oxygen and carbon monoxide (parallel to the rod connecting the centres of atoms of the given molecule) and a parallel body to a tetrahedron (determined by centres of the hydrogen atoms, *cf.* Fig. 1) to methane. Thicknesses of these cores were adjusted to heats of vaporization of pure substances[6]. Values of the geometric functionals R_j, S_j and V_j employed in this paper are given in Table I. This table also contains values of the parameter ε_{ii} adjusted to the liquid volume (obtained from the perturbation expansion for the pure component). The parameter ε_{ij} was determined from the combination rule

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}\,(1 - k_{12})\,, \quad k_{12} = 0\,, \tag{17}$$

TABLE I

Geometric Functionals and the Energy Parameter of the Triangle-Well Convex-Core Potential

Substance	$R_c/10^{-10}$ m	$S_c/10^{-20}$ m^2	$V_c/10^{-30}$ m^3	(ε/k)/K
Ar	1·743	38·18	22·18	113·1
N_2	1·882	43·57	26·32	98·3
O_2	1·790	39·32	22·50	118·0
CO	1·897	44·16	26·79	102·0
CH_4	1·945	46·85	29·55	149·0

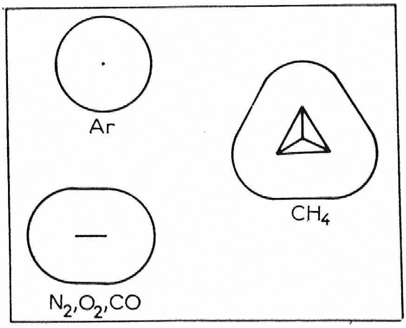

FIG. 1

Convex Cores of the Substances Investigated and the parameter γ was set equal to 0·9 for interactions in all molecular pairs involved.

The perturbation expansion was used for calculating the properties of both pure components (residual Gibbs free energy and enthalpy) and the excess volume of mixture ΔV^{E} at the pressure $P \to 0$ from equation of state (*12*) by an iterative procedure. From the pure liquid volume, V^{liq}, and that of the mixture, V^{mix}, the excess entropy was calculated according to the relation

$$\frac{\Delta S^{\mathrm{E}}}{Nk} = \sum_i x_i \left\{ \ln \frac{V^{\mathrm{mix}}}{V_i^{\mathrm{liq}}} + (\alpha_i^2 - 1) \ln (1 - y_i) - \left(\frac{qs^2}{9nv^2} - 1 \right) \ln (1 - v) + \right. \\ \left. + \left[\frac{3\alpha_i y_i}{(1 - y_i)} - \frac{rs}{n(1 - v)} \right] + \left[\frac{\alpha_i^2 y_i}{(1 - y_i)^2} - \frac{qs^2}{9nv(1 - v)^2} \right] ; \right. \qquad (18)$$

the excess Gibbs free energy G^{E} and excess enthalpy ΔH^{E} follow from expression (*11*). Values of the excess thermodynamic functions in equimolar mixtures are summarized in Table II; for the sake of a comparison, experimental values as well as values obtained from the perturbation theory with the square-well convex-core potential[3] are also reported.

It follows from the comparison in Table II that the procedure employed yields a good prediction of the behaviour of mixtures investigated; however, no unambigu-

TABLE II

The Comparison of the Excess Thermodynamic Functions of the Equimolar Mixtures Calculated from the Perturbation Theory for the Triangle-Well (tr) and Square-Well (sq) Convex-Core Potentials and the Experimental Values[7]

System T/K	$Ar—N_2$ 84	$N_2—O_2$ 77	$N_2—CH_4$ 91	$CO—CH_4$ 91
$\Delta G^{\mathrm{E}}_{\mathrm{tr}}/\mathrm{J\,mol^{-1}}$	23	55	120	101
$\Delta G^{\mathrm{E}}_{\mathrm{sq}}/\mathrm{J\,mol^{-1}}$	44	93	136	109
$\Delta G^{\mathrm{E}}_{\mathrm{exp}}/\mathrm{J\,mol^{-1}}$	34	42	141	117
$\Delta H^{\mathrm{E}}_{\mathrm{tr}}/\mathrm{J\,mol^{-1}}$	32	68	60	55
$\Delta H^{\mathrm{E}}_{\mathrm{sq}}/\mathrm{J\,mol^{-1}}$	55	109	84	70
$\Delta H^{\mathrm{E}}_{\mathrm{exp}}/\mathrm{J\,mol^{-1}}$	50	44	—	106
$\Delta V^{\mathrm{E}}_{\mathrm{tr}}/\mathrm{cm^3\,mol^{-1}}$	−0·14	−0·20	−0·85	−0·66
$\Delta V^{\mathrm{E}}_{\mathrm{sq}}/\mathrm{cm^3\,mol^{-1}}$	−0·22	−0·30	−0·88	−0·64
$\Delta V^{\mathrm{E}}_{\mathrm{exp}}/\mathrm{cm^3\,mol^{-1}}$	−0·18	−0·21	−0·21	−0·33

ous conclusions can be drawn from the comparison between the results for the square-well and triangle-well core potentials: the triangle-well potential gives better results for the first two systems. where the value of k_{12} in relation (*17*) is known to be (for the Kihara central potential) extremely low. The experimental value $k_{12} \approx 0{\cdot}02$ in the central pair interaction models for the other two systems gives in the theory with the triangle-well potential somewhat worse results than with the square-well one. Due to the lack of data on the cross-parameters for convex core potentials, we cannot decide definitely whether the use of the square-well core potential entails a better compensation of errors (due to the model of the intermolecular interaction employed and to the combination rule (*17*)), or whether it is brought about by the approximations used in the derivation of the perturbation term in expansions of the individual thermodynamic functions. A better approximation of the intermolecular interactions by the triangle-well core potential (in comparison with the square-well one) manifested itself in a better agreement between values of parameters ε and known values of the potential energy in the minimum for the simplest substances studied.

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