

EXCESS THERMODYNAMIC FUNCTIONS OF KIHARA-MOLECULE MIXTURES FROM THE SIMPLE PERTURBATION THEORY

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Theoretical relations for excess properties, ΔG^E and ΔH^E , of liquid mixtures whose molecules are representable by convex bodies, were derived from Boublík's perturbation theory and semi-empirical equations for the pair distribution function of a reference system. A non-spherical Kihara potential is considered and the thickness of representative bodies is determined from a generalized Barker-Henderson's theory. Computed results for binary mixtures $N_2 + Ar$, $N_2 + O_2$, $N_2 + CH_4$ and benzene-cyclohexane are in reasonable agreement with the experiment.

In the last few years, there has been a considerable development of perturbation theories as a tool for studying the liquid state. As it is well-known these theories are based on the selection of a reference system, usually related to a hard core potential, similar in some way to the real system. Once the distribution function of such a system is known, it is a simple matter to calculate the perturbation contribution to the Helmholtz energy. The usual reference system for monoatomic fluids is the hard sphere system which provides a physically reasonable model and its distribution function is fairly well-known. However, the selection of the potential and its split-up are not so clear for polyatomic fluids, since distribution functions depend on molecular orientations and are poorly known.

One of the attempts to overcome these difficulties is due to Boublík¹. He assumes potentials where interactions depend only on the shortest distance between cores and uses a pair distribution function averaged over all the orientations. Besides, several analytic expressions in agreement with Monte Carlo results are proposed for pair distribution functions.

It came out that recently derived expressions for pure N_2 gave excellent results¹. On the other hand, simple expressions for distribution functions and very simple potentials, too, have been applied for mixtures of hard convex bodies with a thickness independent of temperature².

The purpose of this work is to calculate excess properties, ΔG^E and ΔH^E , of some binary mixtures applying a realistic potential and taking into account thickness variation with temperature.

THEORETICAL

We consider a system made up of different types of molecules (1, 2, ...) not necessarily spherical. They interact through a Kihara potential with non-spherical core

and geometrical functionals volume, surface and $(4\pi)^{-1}$ (mean curvature) are V_i , S_i and R_i , respectively. Following Boublík¹, we define a reference system and that of representative hard bodies.

According to Weeks–Chandler–Andersen theory (ref.⁴), the perturbation and the reference potentials are:

$$u_{ij}^r = \varepsilon_{ij} \left\{ \left(\frac{q_{ij}}{\varrho} \right)^{12} - 2 \left(\frac{q_{ij}}{\varrho} \right)^6 \right\} + \varepsilon_{ij}, \quad \varrho \leq q_{ij} \quad (1)$$

$$u_{ij}^r = 0, \quad \varrho > q_{ij}$$

$$u_{ij}^p = -\varepsilon_{ij}, \quad \varrho \leq q_{ij} \quad (2)$$

$$u_{ij}^p = \varepsilon_{ij} \left\{ \left(\frac{q_{ij}}{\varrho} \right)^{12} - 2 \left(\frac{q_{ij}}{\varrho} \right)^6 \right\}, \quad \varrho = q_{ij}$$

where ϱ is the shortest distance between the Kihara cores, ε_{ij} is the potential well depth for the species i and j , q_{ij} is defined by

$$u(q_{ij}) = -\varepsilon_{ij} \quad (3)$$

and

$$u = u^r + u^p. \quad (4)$$

The representative hard convex bodies are the parallel bodies with the distance d_{ii} from the Kihara potential cores. This thickness of hard convex bodies is computed from a generalization of Barker–Henderson relation³,

$$d_{ii} = \int_0^{q_{ii}} [1 - \exp(-u_{ii}^r(\varrho)/kT)] d\varrho. \quad (5)$$

The combining rule

$$d_{ij} = (d_{ii} + d_{jj})/2 \quad (6)$$

is assumed to be valid.

Boublík has shown⁴ that taking only the first term in a perturbation expansion, the Helmholtz energy of an actual system is given by

$$\begin{aligned} \frac{F - F^*}{NkT} = & \frac{F^0 - F^*}{NkT} + \frac{n}{2kT} \sum x_i x_j \int_0^\infty u_{ij}^p(\varrho) g_{ij}^0(\varrho^0) S_{i+\varrho+j} d\varrho - \\ & - n x_i x_j g_{ij}^0(0) S_{i+d+j} \left\{ d_{ij} - \int_0^{q_{ij}} [1 - \exp(-\beta u_{ij}^r)] d\varrho \right\}, \quad (7) \end{aligned}$$

where the superscript o refers to the system of representative hard convex bodies, n is the particle number density, x_i the mole fraction of component i , and

$$\begin{aligned} S_{i+o+j} &= S_{ij} + 8\pi R_{ij}\rho + 4\pi\rho^2 = \\ &= S_i + S_j + 8\pi(R_i + R_j)\rho + 8\pi R_i R_j + 4\pi\rho^2. \end{aligned} \quad (8)$$

Let us now define $h_{ij}(\rho)$ as:

$$h_{ij}(\rho) = g_{ij}^o(\rho) - 1 \quad (9)$$

It has been found² that $h_{ij}(\rho)$ may be given approximately by

$$h_{ij}(\rho) = A_{ij} + B_{ij} \frac{S_{ij} + 4\pi\rho R_{ij}}{S_{i+o+j}} \quad \text{for } 0 < \rho < b_{ij} \quad (10)$$

$$h_{ij}(\rho) = 0 \quad \text{for } \rho > b_{ij}$$

with

$$A_{ij} = [1 - g_{ij}^o(0)] \frac{S_{ij} + 4\pi R_{ij} b_{ij}}{4\pi R_{ij} b_{ij} + 4\pi b_{ij}^2} \quad (11)$$

$$B_{ij} = [g_{ij}^o(0) - 1] \frac{S_{ij} + 8\pi R_{ij} b_{ij} + 4\pi b_{ij}^2}{4\pi R_{ij} b_{ij} + 4\pi b_{ij}^2} \quad (12)$$

$$b_{ij} = R_{ij}/g_{ij}^o(0). \quad (13)$$

Several expressions for the Helmholtz energy and the pair distribution function at contact are known; we use those derived by Boublík⁵.

$$g^o(0) = \frac{1}{1-v} + \frac{(S_i T_j + S_j T_i) s + S_i S_j (r-t)}{(1-v)^2 S_{i+j}} + \frac{2S_i S_j g s}{9(1-v)^3 S_{i+j}} \quad (14)$$

$$\frac{F^o - F^*}{NkT} = \left(\frac{qs^2}{9nv^2} - 1 \right) \ln(1-v) + \frac{rs}{n(1-v)} + \frac{qs^2}{9nv(1-v)^2} \quad (15)$$

where

$$T_i = 4\pi R_i^3 / S_i \quad (16)$$

$$Q_i = R_i^2 \quad (17)$$

and for any functional:

$$y = n \sum_i x_i Y_i. \quad (18)$$

It should be pointed out that in Eq. (7), the origin for the potential term is at the Kihara core while for the distribution function term is at surface of the representative hard convex bodies. Since these bodies are parallel to the cores, the relationship between the shortest distances is

$$\varrho_{ij}^0 = \varrho_{ij} - d_{ij}.$$

With this in mind, we define:

$$z = \varrho/q_{ij}; \quad \delta_{ij} = d_{ij}/q_{ij} \quad \text{and} \quad \Delta_{ij} = (d_{ij} + b_{ij})/q_{ij} \quad (19)$$

so that the perturbation potential as a function of z is:

$$\begin{aligned} u_{ij}^p(z) &= -\varepsilon_{ij} & z \leq 1 \\ u_{ij}^p(z) &= \varepsilon_{ij}(z^{-12} - 2z^{-6}) & z > 1 \end{aligned} \quad (20)$$

and the equation (1) is written as:

$$\begin{aligned} \frac{F - F^*}{NkT} &= \frac{F^0 - F^*}{NkT} + \frac{n}{2kT} \sum_{i,j} x_i x_j q_{ij} \varepsilon_{ij} \left\{ - \int_{\delta_{ij}}^1 g_{ij}^0(\varrho - d) S_{i+\varrho+j} dz + \right. \\ &+ \int_1^{\Delta_{ij}} (z^{-12} - 2z^{-6}) g_{ij}^0(\varrho - d) S_{i+\varrho+j} dz + \int_{\Delta_{ij}}^{\infty} (z^{-12} - 2z^{-6}) S_{i+\varrho+j} dz \left. \right\} - \\ &- n x_i x_j g_{ij}^0(0) S_{i+d_{ij}+j} \left\{ d_{ij} - \int_0^{\varrho_{ij}} [1 - \exp(-\beta u_{ij}^r(\varrho))] d\varrho \right\} \end{aligned} \quad (21)$$

as long as $\Delta_{ij} > 1$, the most common situation. Carrying out the integration, we get

$$\begin{aligned} \frac{F - F^*}{NkT} &= \frac{F^0 - F^*}{NkT} + \frac{n}{2kT} \sum_{i,j} x_i x_j q_{ij} \varepsilon_{ij} \left[(\alpha_{ij} - p_{ij}) \left(\frac{2\Delta_{ij}^{-3}}{3} - \frac{\Delta_{ij}^{-9}}{9} \right) + \right. \\ &+ (\beta_{ij} - n_{ij}) \left(\frac{\Delta_{ij}^{-4}}{2} - \frac{\Delta_{ij}^{-10}}{10} \right) + (\gamma_{ij} - m_{ij}) \left(\frac{2\Delta_{ij}^{-5}}{5} - \frac{\Delta_{ij}^{-11}}{11} \right) + \\ &\left. + \frac{\alpha_{ij}}{3} \left(\delta_{ij}^3 - \frac{8}{3} \right) + \frac{\beta_{ij}}{2} \left(\delta_{ij}^2 - \frac{9}{5} \right) + \gamma_{ij} \left(\delta_{ij} - \frac{72}{11} \right) - M \right], \end{aligned} \quad (22)$$

where

$$m_{ij} = S_{ij} + 4\pi d_{ij}^2 - 8\pi R_{ij} d_{ij} \quad (23)$$

$$n_{ij} = 8\pi q_{ij} R_{ij} - 8\pi d_{ij} q_{ij} \quad (24)$$

$$p_{ij} = 4\pi q_{ij}^2 \quad (25)$$

$$t_{ij} = S_{ij} - 4\pi R_{ij} d_{ij} \quad (26)$$

$$v_{ij} = 4\pi R_{ij} q_{ij} \quad (27)$$

$$\alpha_{ij} = (A_{ij} + 1) p_{ij} \quad (28)$$

$$\beta_{ij} = n_{ij}(A_{ij} + 1) + v_{ij}(g_{ij}(0) - 1 - A_{ij}) \quad (29)$$

$$\gamma_{ij} = m_{ij}(A_{ij} + 1) + t_{ij}(g_{ij}(0) - 1 - A_{ij}) \quad (30)$$

$$M = n x_i x_j g_{ij}^0(0) S_{i+d_{ij}+j} \left\{ d_{ij} - \int_0^{q_{ij}} [1 - \exp(-\beta u_{ij}^r)] d\varrho \right\}. \quad (31)$$

TABLE I

Parameters of the Kihara Pair Potential and Geometric Functionals of Cores

Substance	N ₂	O ₂	Ar	CH ₄	Benzene	Cyclohexane
Ref.	6	7	8	9	10	10
q, 10 ⁻¹⁰ m	3.60	3.64	3.307	3.15	2.96	3.052
(ε/k), K	117	130	147.2	226	852.3	950.5
R _c , 10 ⁻¹⁰ m	0.2325	0.111	0.164	0.4974	1.167	0.853
S _c , 10 ⁻²⁰ m ²	0	0	0.338	1.38	14.22	3.42
V _c , 10 ⁻³⁰ m ³	0	0	0.019	0.084	2.49	3.32

TABLE II

Excess Thermodynamic Functions for Equimolar Mixtures

System	Ar + N ₂	N ₂ + CH ₄	N ₂ + O ₂	C ₆ H ₆ + C ₆ H ₁₂
T, K	84	91	77	298.15
ΔG _{calc} ^E , J mol ⁻¹	60	197	41	375
ΔG _{exp} ^E , J mol ⁻¹	34	141	42	360
ΔH _{calc} ^E , J mol ⁻¹	43	157	119	339
ΔH _{exp} ^E , J mol ⁻¹	50	—	44	828

The main interest of Eq. (2) is that now we can obtain Helmholtz energy easily from the parameters and the thickness of representative hard convex bodies.

RESULTS AND DISCUSSION

Eq. (22) has been applied to calculate the excess thermodynamic functions of four binary mixtures Ar-N₂ at 84 K, N₂-O₂ at 77 K, N₂-CH₄ at 91 K and benzene-cyclohexane at 298.15 K. Parameters of the Kihara pair potential and the geometric functionals of assumed cores are given in Table I.

Combining rules $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$ and $q_{ij} = \frac{1}{2}(q_{ii} + q_{jj})$ were considered and ΔG^E and ΔH^E calculated under assumption of $\Delta V^E = 0$.

Values of excess functions ΔG^E and ΔH^E of equimolar mixtures determined from Eq (22) (ΔH^E was calculated by numerical derivation) are compared with experimental data in Table II.

Table II shows that the calculated value for ΔH^E and especially for ΔG^E agree fairly well with experiment. It is seen that systems of large complex molecules are described by the theory with similar degree of accuracy as systems of small nearly spherical molecules. This fact gives evidence in favor of considering the perturbation theory of convex molecules as proper tool of describing general systems of non-polar compounds. Deviations are due before all to the used combining rules and the oversimplified relations for the average correlation function.

It appears that the use of more detailed description of intermolecular interactions does not result in an improve of the agreement in excess thermodynamic functions; this follows from the comparison with previous studies of one of the authors². Therefore, it seems necessary to employ the more sophisticated relations for the average correlation functions (*e.g.* that of ref.⁴) and more complicated treatment including better combining rules for interaction parameters when seeking out improvements in description of molecular mixture behaviour.

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