

FIRST-ORDER PERTURBATION EXPANSION FOR A MIXTURE OF NONSPHERICAL MOLECULES

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The perturbation expansion formulated for a system of nonspherical and nonpolar molecules was employed for determining excess thermodynamic functions of binary solutions. Molecular interactions were described by a core square-well pair potential; the system of hard convex bodies was used as the reference. Thermodynamic functions of the reference system were calculated from an improved version of the scaled particle (SPT) equation of state; the dependence of the averaged correlation function on distance was approximated by a simple relation which represents well the principal descending part of this curve. Its value at contact was also determined from improved SPT expressions.

Perturbation theories of fluids constitute presently a proper tool for the description of one- and multicomponent systems of simple liquids. Recently^{1,2} we have formulated a perturbation expansion which may be used for the description of equilibrium behaviour of systems formed by nonpolar and nonspherical molecules interacting *via* a Kihara-type pair potential³ (which depends only on the shortest distance between surfaces of two hard convex cores of the interacting molecules).

For Kihara-type pair potentials, the system of hard convex bodies (corresponding with the given type of molecules) represents a natural choice for the reference system; for such a system, however, only the equation of state and the averaged value of the correlation function g^{av} at contact have been found. In view of this limited knowledge of the course of g^{av} , the molecular interactions were interpreted in our earlier work² in terms of an extremely simplified model of the pair potential, namely through the core square-well potential with a very narrow well, so that the particle distribution may be described for this range by the value of the correlation function at contact.

THEORETICAL

Here, the course of the averaged correlation function is approximated for all distances $q > 0$ (q is the shortest distance between surfaces of two convex bodies); this fact allows one to describe the intermolecular interactions by the common core square-well potential with a finite width of the well, or possibly by other more realistic potentials.

We will use the core square-well potential in the form

$$\begin{aligned} w_{ij}(\varrho) &= \infty & \text{for } \varrho < 0 \\ &= -\varepsilon_{ij} & 0 < \varrho < a_{ij} \\ &= 0 & \varrho > a_{ij}, \end{aligned} \quad (1)$$

with a_{ij} being the characteristic distance which specifies the range of the attractive forces.

The perturbation potential is then given by

$$\begin{aligned} w_{ij}^p(\varrho) &= 0 & \text{for } \varrho < 0 \\ &= w_{ij}(\varrho) & \varrho > 0. \end{aligned} \quad (2)$$

With our choice of the reference system and the perturbation, the first order perturbation expansion of the free energy F assumes the form

$$\frac{F}{NkT} = \frac{F^0}{NkT} + \frac{n}{2kT} \int_0^\infty w_{ii}^p(\varrho) g_{ii}^{0,av}(\varrho) \mathcal{S}_{i+\varrho+i} d\varrho, \quad (3)$$

whereas for a mixture we can write

$$\frac{F_s}{NkT} = \frac{F_s^0}{NkT} + \frac{n}{2kT} \sum_{i,j} x_i x_j \int_0^\infty w_{ij}^p(\varrho) g_{ij}^{0,av}(\varrho) \mathcal{S}_{i+\varrho+j} d\varrho. \quad (4)$$

In these equations, superscript 0 denotes reference system functions and $\mathcal{S}_{i+\varrho+j}$ is the surface of a convex body formed by the centre of a hard convex particle j when moving with respect to a fixed particle i provided that the shortest distance between their surfaces is constant and equal to ϱ ; N is the number of molecules in a system of volume V at temperature T , n is the number density and k Boltzmann's constant.

As in this approximation the magnitude as well as shape of representative hard convex bodies does not depend on temperature, the function $g^{0,av}$ is also temperature-independent. It then follows from Eqs (3) and (4) that the configurational energy is given by the first order perturbation term in the free energy expansion, *i.e.*

$$U_i - U_i^* = U_i - U_i^0 = F_i - F_i^0, \quad (5)$$

resp.

$$U_s - U_s^* = F_s - F_s^0; \quad (6)$$

the entropy of the examined system is then equal to the reference system entropy

$$S_i - S_i^0 = 0, \quad S_s - S_s^0 = 0. \quad (7), (8)$$

Obviously it holds

$$\Delta S^E = \Delta S^{0E}; \quad (9)$$

the excess entropy of the examined system can be thus determined from the equation of state of reference hard convex bodies by employing the relation

$$(S^0 - S^*)/Nk = - \int_0^n n^{-1}(P^0/nkT - 1) dn, \quad (10)$$

and from a similar expression for the mixture. [The asterisk in Eqs (5)–(10) denotes functions of the ideal gas.]

The compressibility factor of the system of hard convex bodies, P^0/nkT , was calculated from a modified SPT equation, which has been derived recently⁴. For a one-component system we can write

$$P^0/nkT = [1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3]/(1 - y)^3, \quad (11)$$

where y denotes the ratio of volumes of the convex body and the system,

$$y = n\mathcal{V}_i = N\mathcal{V}_i/V, \quad (12)$$

and the parameter α , which measures the nonsphericity of the body, is given by the volume \mathcal{V}_i , surface \mathcal{S}_i and $(1/4\pi)$ –multiple of the mean curvature integral \mathcal{R}_i of the convex body,

$$\alpha = \mathcal{R}_i\mathcal{S}_i/3\mathcal{V}_i. \quad (13)$$

(For a sphere, $\alpha = 1$ and Eq. (11) passes to the equation of state by Carnahan and Starling⁵.)

Similarly, the pressure in a mixture of several sorts of hard convex bodies may be determined from the relation

$$\frac{P_s^0}{nkT} = \frac{1}{(1 - v)} + \frac{rs}{n(1 - v)^2} + \frac{qs^2(3 - v)}{9n(1 - v)^3}, \quad (14)$$

with

$$r = n \sum_i x_i \mathcal{R}_i, \quad q = n \sum_i x_i \mathcal{R}_i^2, \quad s = n \sum_i x_i \mathcal{S}_i, \quad v = n \sum_i x_i \mathcal{V}_i. \quad (15)–(18)$$

The following expression for the excess entropy of the mixture is then obtained from Eqs (9)–(18)

$$\frac{\Delta S^E}{Nk} = \sum_i x_i \left\{ \ln \frac{V_s}{V_i} + \left[(\alpha_i^2 - 1) \ln(1 - y_i) - \left(\frac{qs^2}{9nv^2} - 1 \right) \ln(1 - v) \right] + \left[\frac{3\alpha_i y_i}{(1 - y_i)} - \frac{rs}{n(1 - v)} \right] + \left[\frac{\alpha_i^2 y_i}{(1 - y_i)^2} - \frac{qs^2}{9nv(1 - v)^2} \right] \right\}. \quad (19)$$

For determining the first order perturbation term in the free energy expansion which is given by the integral from the product of the perturbation potential and the averaged correlation function, it will be useful to introduce a function $h^0(\varrho)$ which is an analogue of the total correlation function for hard spheres; this function is defined by

$$h^0(\varrho) = g^{0av}(\varrho) - 1. \quad (20)$$

Because only contact values of the function $h^0(\varrho)$, resp. $g^{0av}(\varrho)$, are available for the system of hard convex bodies^{1,2,4}, we were seeking for a simple and accurate approximation for the descending part of the curve $h^0(\varrho)$ (for $\varrho > 0$). The approximation

$$h^0(x) = A + B/x \quad \text{for } 1 < x < x_m \\ = 0 \quad \text{for } x > x_m \quad (21)$$

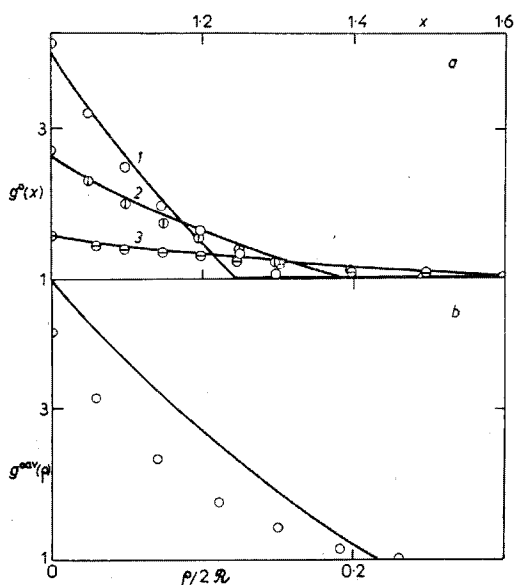


FIG. 1

Comparison of the Approximate Course of the Radial Distribution Function $g^0(x)$ and the Averaged Correlation Function $g^{0av}(\varrho)$ with Pseudoexperimental Data

a $\alpha = 1$; \circ $y = 0.419$, \oplus $y = 0.314$, \odot $y = 0.157$; b $\alpha = 1.5$; \circ $y = 0.4$.

with $x_m = 1 + 1/g^0(1)$ has proved to be satisfactory for the hard sphere system; A and B may be determined from the contact value of the radial distribution function (e.g. from the Carnahan–Starling equation of state) and from the condition $h^0(x_m) = 0$. The approximate course of the function $g^0(x)$ for hard spheres at three different densities is compared on Fig. 1a with pseudoexperimental data; good agreement at all densities is obvious from this comparison.

Analogously, the following approximation for the function $h^0(\varrho)$ was used for hard convex bodies

$$\begin{aligned} h_{ij}^0(\varrho) &= A_{ij} + B_{ij}(\mathcal{S}_{i+j} + 4\pi\varrho\mathcal{R}_{i+j})/\mathcal{S}_{i+\varrho+j} \quad \text{for } 0 < \varrho < b_{ij} \\ &= 0 \quad \text{for } \varrho > b_{ij}, \end{aligned} \quad (22)$$

where

$$b_{ij} = \mathcal{R}_{i+j}/g_{ij}^{0\text{av}}(0) \quad (23)$$

and for A_{ij} and B_{ij} it holds

$$A_{ij} = [1 - g_{ij}^{0\text{av}}(0)] (\mathcal{S}_{i+j} + 4\pi\mathcal{R}_{i+j}b_{ij}) / (4\pi\mathcal{R}_{i+j}b_{ij} + 4\pi b_{ij}^2), \quad (24)$$

$$B_{ij} = [g_{ij}^{0\text{av}}(0) - 1] (\mathcal{S}_{i+j} + 8\pi\mathcal{R}_{i+j}b_{ij} + 4\pi b_{ij}^2) / (4\pi\mathcal{R}_{i+j}b_{ij} + 4\pi b_{ij}^2). \quad (25)$$

The course of the function $g^{0\text{av}}(\varrho)$ approximated by relation (22) is compared on Fig. 1b with preliminary results of our Monte-Carlo study on the behaviour of hard spherocylinders with the parameter $\alpha = 1.5$ at $y = 0.4$. Obviously, the approximate $g^{0\text{av}}(\varrho)$ values are in this rather extreme case higher than the pseudoexperimental ones. This higher difference is brought about by the inaccurate approximation of the averaged correlation function at contact resulting from the use of the modified SPT relation.

On substituting the approximate expression for $g^{0\text{av}}(\varrho)$ into the integral in Eq. (4) and taking into account relation (20), the first order perturbation term for the mixture is equal to

$$\begin{aligned} \frac{\langle W_s \rangle}{NkT} &= -\frac{n}{2kT} \sum_{i,j} x_i x_j \varepsilon_{ij} \left[\int_0^{a_{ij}} \mathcal{S}_{i+\varrho+j} d\varrho + A_{ij} \int_0^{b_{ij}} \mathcal{S}_{i+\varrho+j} d\varrho + \right. \\ &\quad \left. + B_{ij} \int_0^{b_{ij}} (\mathcal{S}_{i+j} + 4\pi\varrho\mathcal{R}_{i+j}) d\varrho \right]; \end{aligned} \quad (26)$$

and a similar expression might be obtained for a pure component.

In the last equation the functionals $\mathcal{S}_{i+\varrho+j}$ and $\mathcal{R}_{i+\varrho+j}$ can be expressed through geometric functionals of individual convex bodies:

$$\mathcal{S}_{i+\varrho+j} = (\mathcal{S}_i + \mathcal{S}_j + 8\pi\mathcal{R}_i\mathcal{R}_j) + 8\pi(\mathcal{R}_i + \mathcal{R}_j)\varrho + 4\pi\varrho^2, \quad (27)$$

and

$$\mathcal{R}_{i+\ell+j} = \mathcal{R}_i + \mathcal{R}_j + \ell. \quad (28)$$

RESULTS AND DISCUSSION

The proposed procedure was used for determining excess thermodynamic functions of four binary model systems whose molecules may be easily visualized as convex bodies: we have studied the systems $\text{N}_2 + \text{Ar}$ at 84K, $\text{O}_2 + \text{Ar}$ at 84K, $\text{N}_2 + \text{O}_2$ at 77K and $\text{N}_2 + \text{CH}_4$ at 91K. Molecules of the pure substances can be represented by convex bodies, whose core is a point in the case of argon, a line segment connecting centres of two atoms in the case of nitrogen and oxygen or a regular tetrahedron joining midpoints of CH bonds in the case of methane. The thickness of parallel convex bodies as well as the depth of the potential well was adjusted to fit the P - V - T behaviour of the given liquid. Simultaneously we have assumed that the parameter a_{ii} , which determines the range of the attractive forces, is equal to

$$a_{ii} = 0.9\mathcal{R}_{i+i}. \quad (29)$$

The employed values of the geometric functionals of convex cores, \mathcal{R}_c , \mathcal{S}_c , and \mathcal{V}_c , thickness of the parallel convex bodies and values of ϵ/k are given in Table I. Geometric functionals of representative hard convex bodies were calculated according to the following relations

$$\mathcal{R}_i = \mathcal{R}_c + \xi, \quad (30)$$

$$\mathcal{S}_i = \mathcal{S}_c + 8\pi\mathcal{R}_c\xi + 4\pi\xi^2, \quad (31)$$

$$\mathcal{V}_i = \mathcal{V}_c + \mathcal{S}_c\xi + 4\pi\mathcal{R}_c\xi^2 + \frac{4}{3}\pi\xi^3. \quad (32)$$

TABLE I

Geometric Functionals of Cores, Thickness of Parallel Convex Bodies (ξ) and Parameter ϵ/k in the Interaction Potential

Substance	\mathcal{R}_c , Å	\mathcal{S}_c , Å ²	\mathcal{V}_c , Å ³	ξ , Å	(ϵ/k) , K ⁻¹
Ar	0.0	0.0	0.0	1.743	63.86
N ₂	0.273	0.0	0.0	1.608	52.57
O ₂	0.275	0.0	0.0	1.515	67.27
CH ₄	0.407	1.379	0.084	1.538	81.63

The thermodynamic properties of the mixture (for $P \rightarrow 0$) were computed on the assumption of validity of the following mixing rule

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{0.5}. \quad (33)$$

In calculating the thermodynamic functions of a mixture at a given composition, the first step consisted in determining the volume V_s for $P \rightarrow 0$ from the equation

$$\begin{aligned} \frac{P - P^0}{nkT} = & -\frac{n}{2kT} \sum_{i,j} x_i x_j \varepsilon_{ij} \{ \mathcal{L}_{i+j} \mathcal{R}_{i+j} \delta + 4\pi \mathcal{R}_{i+j}^3 (\delta^2 + \delta^3/3) + \\ & + (g_{ij} - 1) [\mathcal{L}_{i+j} \mathcal{R}_{i+j} (3g_{ij}^2 + 4g_{ij}) + 4\pi \mathcal{R}_{i+j}^3] / 6g_{ij}^2 (g_{ij} + 1) + n(\partial g_{ij} / \partial n) \cdot \\ & \cdot [\mathcal{L}_{i+j} \mathcal{R}_{i+j} (2g_{ij}^3 + 8g_{ij}^2 + 4g_{ij}) + 8\pi \mathcal{R}_{i+j}^3 (-g_{ij}^2 + g_{ij} + 1)] / 6g_{ij}^2 (g_{ij} + 1)^2 \} \quad (34) \end{aligned}$$

in which the symbol δ stands for the ratio a_{ij}/\mathcal{R}_{i+j} .

This computed volume of the mixture was then employed for determining the excess volume ΔV^E and subsequently also ΔS^E and ΔG^E . A comparison between calculated excess thermodynamic functions of equimolar mixtures and experimental data⁶ is in Table II.

In conclusion it may be stated that the employed first order perturbation theory, the representation of intermolecular interactions by the core square-well potential and the simple approximation of the averaged correlation function lead to a quanti-

TABLE II

Comparison of Calculated and Experimental Values of Excess Thermodynamic Functions for Equimolar Mixtures

System	N ₂ + Ar	O ₂ + Ar	N ₂ + O ₂	N ₂ + CH ₄
<i>T</i> , K	84	84	77	91
$\Delta G^E / \text{J mol}^{-1}$	44	5	93	136
$\Delta G_{\text{exp}}^E / \text{J mol}^{-1}$	34	37	42	141
$\Delta H^E / \text{J mol}^{-1}$	55	5	109	84
$\Delta H_{\text{exp}}^E / \text{J mol}^{-1}$	50	60	44	—
$\Delta V^E / \text{ml mol}^{-1}$	-0.22	-0.02	-0.30	-0.88
$\Delta V_{\text{exp}}^E / \text{ml mol}^{-1}$	-0.18	0.14	-0.21	-0.21

tative description of systems containing nonpolar and nonspherical molecules. Agreement between the calculated and direct experimental excess thermodynamic functions may be considered as adequate to the degree of the approximation used.

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