

## Equilibrium behaviour of non-spherical non-polar molecule fluids

Tomáš Boublík

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

**Abstract** - Perturbation theory of convex molecule fluids is outlined and applied to correlate orthobaric data of several convex molecule systems. Calculated data from the fitting procedure are compared with results of the variant of the perturbation theory proposed for the two-centre LJ systems. A modification of the convex-molecule perturbation theory for the gaussian overlap fluid is given and obtained thermodynamic functions compared with the simulation data. The accurate hard body equations of state are listed and mixing rules for their parameters discussed.

### INTRODUCTION

Perturbation theories of non-spherical non-polar molecule fluids offer ever improving description of the equilibrium behaviour of a large group of real liquids and their mixtures. Besides the direct application of perturbation expansions to evaluate thermodynamic functions of molecular fluids the theory also provides arguments for a further improvement of the so-called augmented van der Waals equations of state and mixing (eventually also combining) rules for their parameters.

The methods proposed for simple fluids form a basis for the development of the perturbation theory of non-spherical molecule fluids. Two variants of the theory have been widely used - that due to Barker and Henderson (B-H), (ref. 1.) extended to mixtures by Leonard et al. (ref. 2.) and the blip-function approach of Weeks-Chandler and Andersen (WCA) (ref. 3.). In both these variants soft spheres are taken as a reference and attractive (plus the remaining part of repulsive) forces contribute to perturbation terms. The thermodynamic behaviour of the reference is determined via the properties of the representative hard spheres whose diameter depends on temperature in the former- and on temperature and density in the latter case. The first-order WCA theory is very accurate at high densities (for the packing fraction  $\eta > 0.4$ ); it is less accurate at low and medium densities. The second-order B-H theory is only slightly less accurate at the highest densities but superior at lower densities.

### PAIR POTENTIALS OF NON-SPHERICAL MOLECULES

Description of the equilibrium behaviour of the non-polar molecule fluids depends on the model employed to characterize pair interactions of (generally) non-spherical molecules. Three models have been used: i) the multicentre (site-site) potential, ii) Kihara generalized pair potential iii) gaussian overlap potential.

The multicentre pair potential,  $u(1,2)$ , given by the formula (ref. 4.)

$$u(1,2) = 4 \sum_{\alpha, \gamma} \epsilon_{\alpha\gamma} [(\sigma_{\alpha\gamma}/r_{\alpha\gamma})^{12} - (\sigma_{\alpha\gamma}/r_{\alpha\gamma})^6] \quad (1)$$

[where  $\alpha$  denotes centres on molecule 1 and  $\gamma$  those on molecule 2] offers the most detailed description of molecular interactions. The main advantage of the potential manifests itself in simulation studies where the determination of  $u(1,2)$  is simple. Even simpler for this purpose is the gaussian overlap model (GO)

$$u_G(1,2) = 4 \epsilon(\vec{u}_1, \vec{u}_2, \vec{\tau}) \{ [\sigma(\vec{u}_1, \vec{u}_2, \vec{\tau})/r]^2 - [\sigma(\vec{u}_1, \vec{u}_2, \vec{\tau})/r]^6 \} \quad (2)$$

If  $\chi = (\lambda^2 - 1)/(\lambda^2 + 1)$  and  $\lambda$  is the axis ratio

$$\epsilon(\vec{u}_1, \vec{u}_2, \vec{\tau}) = \epsilon_0 \quad (\text{GOCE}) \quad (3)$$

$$\sigma(\vec{u}_1, \vec{u}_2, \vec{\tau}) = \sigma_0 \left[ 1 - \frac{\chi}{2} \left\{ \frac{(\vec{\tau}\vec{u}_1 + \vec{\tau}\vec{u}_2)^2}{1 + \chi(\vec{u}_1\vec{u}_2)} + \frac{(\vec{\tau}\vec{u}_1 - \vec{\tau}\vec{u}_2)^2}{1 - \chi(\vec{u}_1\vec{u}_2)} \right\} \right]^{-1/2} \quad (4)$$

In this model, however, the shape of the molecule can be either prolate or oblate ellipsoid of revolution.

In the generalized Kihara potential (ref. 6.)

$$u(1,2) = u(s) = 4\epsilon_K [(\sigma_K/s)^{12} - (\sigma_K/s)^6] \quad (5)$$

The shape of a molecule - which reflects repulsive forces - can be modelled by any convex model. One can say that the Kihara pair potential reproduces in a detailed way the repulsive forces whereas some kind of averaging of the effect of attractive forces takes place. Simulations of other model systems than the rod-like molecule fluids are quite involved; on the other hand the formulation of the perturbation theory is - due to the fact that the potential depends only on one variable,  $s$  - very simple.

### PERTURBATION THEORY OF NON-SPHERICAL MOLECULE FLUIDS

For the multicentre pair potential Kohler and Fischer (refs. 7,8) proposed a perturbation method which was an extension of the WCA blip-function approach. For the given orientation  $\vec{\omega}_1 \vec{\omega}_2$  the WCA-split is considered,

$$u^0(r\vec{\omega}_1\vec{\omega}_2) = u(r\vec{\omega}_1\vec{\omega}_2) - u_{\min}(r\vec{\omega}_1\vec{\omega}_2) \quad r < r_{\min}(r\vec{\omega}_1\vec{\omega}_2) \\ = 0 \quad r > r_{\min}(r\vec{\omega}_1\vec{\omega}_2) \quad (6)$$

and

$$u^p(r\vec{\omega}_1\vec{\omega}_2) = u_{\min}(r\vec{\omega}_1\vec{\omega}_2) \quad r < r_{\min}(r\vec{\omega}_1\vec{\omega}_2) \\ = u(r\vec{\omega}_1\vec{\omega}_2) \quad r > r_{\min}(r\vec{\omega}_1\vec{\omega}_2) \quad (7)$$

Properties of the reference are determined via the hard body equation of state applied to hard dumbbells (or other fused hard-sphere models) with the same site-site distance as that of the considered molecule and with the diameter of the site sphere obtained from the blip-function relationship

$$\int Y [\langle \exp(-\beta u^0) \rangle - \langle \exp(-\beta u^{\text{HD}}) \rangle] d\vec{r} = 0 \quad (8)$$

The background correlation function,  $Y$ , corresponds to the soft-body spherically symmetric potential,  $\phi(r)$ , for which

$$\exp[-\beta\phi^0] = \langle \exp[-\beta u^0(r\vec{\omega}_1\vec{\omega}_2)] \rangle \quad (9)$$

The function  $Y$  is evaluated from the Percus-Yevick integral equation (P-Y); the molecular correlation function,  $g(r\vec{\omega}_1\vec{\omega}_2)$  in the perturbation integral is then approximated by

$$g(r\vec{\omega}_1\vec{\omega}_2) = \exp[-\beta u^0(r\vec{\omega}_1\vec{\omega}_2)] Y(r) \quad (10)$$

Only the first-order perturbation term is considered in this theory,

$$F_1/NKT = (\rho/2KT) \int \langle u^p(r\vec{\omega}_1\vec{\omega}_2) \exp[-\beta u^0(r\vec{\omega}_1\vec{\omega}_2)] \rangle Y(r) d\vec{r} \quad (11)$$

where symbol  $\langle \rangle$  denotes averaging over all orientations which - contrary to that in the Kihara potential - is related to centre-to-centre distance. The perturbation method for the multicentre potential was applied to several systems of diatomic molecules and highly symmetric polyatomic molecules (like  $\text{CCl}_4$  or  $\text{SF}_6$ ) and to mixtures of spherical and linear molecules (refs. 9,10).

The basic relationships of the perturbation theory of the convex (rod-like) molecules can be found in ref. 11. Recently, two variants of the theory have been employed in our laboratory: in the former (ref. 12) we considered the second-order perturbation expansion (for the Helmholtz energy and pressure) in the macroscopic compressibility approximation (mc) of the WCA-hybrid approach (the WCA-split of the pair potential into the reference and perturbation part in combination with the  $\beta$ -H-like determination of the thickness of representative hard convex body, hcb). The Helmholtz energy is

$$(F-F^{\text{hcb}})/NKT = (\rho/2KT) \int_d^\infty u^p(s) g^{\text{hcb}}(s) S_{1+s+2} ds - \\ - (\rho/4KT)(\partial\rho/\partial P)^{\text{hcb}} \int_d^\infty [u^p(s)]^2 g^{\text{hcb}}(s) S_{1+s+2} ds \quad (12)$$

Perturbation integrals included in the first and second term of Eq (12), were each separated into two parts at  $s = 1.2 \sigma$ ; these parts were evaluated numerically and the obtained values fitted by polynomials. The resulting expressions were then employed to describe the equilibrium behaviour of pure fluids. The same equation of state and expression for the Helmholtz energy were used to characterize both the liquid and vapour part of the coexistence curve; orthobaric densities along the coexistence curve were used to adjust parameters of the Kihara potential of 28 compounds. As a result of the use of the same expression for the both

branches of the coexistence curve the method enables to describe the equilibrium behaviour up to high reduced temperatures  $T^* \approx 0.9$ ; values of the parameters (mainly the size of the core) differ slightly from those obtained by the variant described in next part. In the latter variant of the perturbation theory (of the convex molecule fluids) the extension of the Barker-Henderson theory to molecular fluids is employed (ref. 13). The representative hard convex bodies are parallel bodies to the convex cores with a thickness obtained from

$$\int_0^{\sigma} \{ \exp[-\beta u^{hcb}] - \exp[\beta u^0] \} S_{i+s+i} ds = 0 \quad (13)$$

[Here  $S_{i+s+i}$  is the mean surface area of two convex cores with the surface-to-surface distance,  $s$ . The hard convex body equation of state for the given representative model yields the reference residual Helmholtz energy. To determine the first-order perturbation term,  $F_1$ ,

$$F_1/NkT = (\rho/2kT) \int_{\sigma}^{\infty} u^p(s) g^{hcb}(s) S_{i+s+i} ds \quad (14)$$

we express first the average correlation function,  $g^{hcb}$ , in terms of the total correlation function,  $h^{hcb} = g^{hcb} - 1$ , and split the integral in Eq (14) into two parts, the larger of which can be easily determined analytically. The total correlation function,  $h^{hcb}$ , was approximated on the basis of the  $h^{ehs}$  - function of the equivalent hard spheres, (ehs, i.e. spheres of the same volume as the studied convex bodies),

$$h^{hcb}(t) = (S^{hcb}/S^{ehs}) h^{ehs}(x); \quad x = 1+t/(1+R_i^*+R_j^*), \quad (15)$$

(where  $R^* = R/d$ ,  $S^* = S/d^2$  and  $R$ ,  $S$ ,  $V$  are the mean curvature integral/ $4\pi$ , surface area and volume of the core). It was shown formerly that the approximation is very accurate for two typical hard convex bodies, prolate and oblate hard spherocylinders and works well also in the case of mixtures. The above approximation was employed already in the former variant. Here we substitute  $h^{ehs}(x) = h^{PY}(x) |h^{exact}(1)/h^{PY}(1)|$ , where symbol P-Y denotes the Percus-Yevick approximation (to the Ornstein-Zernicke equation) which leads to the analytic Laplace transforms of the function  $xg(x)$  or  $xh(x)$ . To make full use of this fact we substitute the double Yukawa (2-Y) pair potential

$$u_{2Y}(x) = (\epsilon/x) \{ \exp[-A(x-1)] - \exp[-B(x-1)] \}, \quad x = r/\sigma \quad (16)$$

for the Kihara function in the second part of the perturbation integral. In this way a part of the integral (containing  $h^{hcb}$ ) can be expressed analytically as a sum of differences in the Laplace transforms, corresponding to parameters A, B of the 2-Y potential, plus a correction term (due to the fact that the lower bond of the perturbation integral equals  $\sigma$  and not twice the thickness of the representative hard body). Thus,

$$F_1/NkT = (2\pi\sigma^3\rho/T^*) [Q + \sum k_n w_n + w] \quad (17)$$

$$-Q = (8/9) + 4R^*(3/5) + 2(S^*/4\pi + R^{*2})(24/55) \quad (18)$$

$$w = \frac{h^{hcb}(1)}{h^{ehs}(1)} h^{ehs}(1+\delta) \int_{d/\sigma}^1 u^p(s) S_{i+s+i} ds \quad (19)$$

and

$$w_k = L\{xh(x)\} (I') \quad (20)$$

Similarly, the perturbation expansion of the compressibility factor can be written in an analytic form, too. The relationships for the Helmholtz energy and pressure make it possible to determine quickly the coexistence curve without any intermediate procedure of fitting numerical data.

In the previous study (ref. 13) we adjusted two parameters of the Kihara pair potential ( $\epsilon$  and  $\sigma$ ) to the saturated liquid properties of pure compounds while determining the other parameters from the bond lengths and angles. The perturbation expansion was used to describe the liquid branch of the coexistence curve whereas the vapour phase was characterized by the virial expansion including the second virial coefficient. The results and some interrelations between the Kihara and 2-centre Lennard-Jones parameters were given in ref. 13.

Recently we have modified this approach by including the approximate third virial coefficient (only for the repulsive forces) and adjusting three parameters, i.e.  $\epsilon$ ,  $\sigma$  and size of the spherical core or length of the rod-like molecule, etc. As a result better agreement of the calculated and experimental coexistence curves are found, see Fig. 1 where the coexistence curve of argon is shown. In Figs 2 - 4 the per cent deviations in pressure and density vs. temperature for Ar, CO<sub>2</sub> and ethane are depicted. For comparison the data found within Kohler-Fischer perturbation theory are given, too. The agreement is very good even for more complex molecules like carbon tetrachloride and benzene.

TABLE 1. Excess thermodynamic functions of the equimolar Xe-C<sub>2</sub>H<sub>6</sub> system at 161 K for  $k_{12} = 1.0$ 

	$G^E(\text{J/mol})$	$H^E(\text{J/mol})$	$V^E(\text{cm}^3)$
Convex pert. theory (2 pars)	-2	-17	-0.04
Convex pert. theory (3 pars)	-32	-72	-0.08
Multicentre part. theory	-113	-193	-0.36
Experimental (ref. 10)	-29	-52	-0.12

One can see that the recent variant of the perturbation method for convex molecules works at least with the same quality as the theory of multicentre fluids. By introducing the non-zero core (in the case of spherical molecules) while still considering 12-6 function we can reach the same effect as Fischer obtained by modifying the pair potential, e.g. by introducing the 24-6 form. The analytic form of the perturbation expansion offers a deeper insight in the molecular fluid behaviour; the range of the reduced temperatures can be larger then in the case of the multicentre perturbation theory.

The perturbation theory of convex molecule fluids was extended (ref. 14) to mixtures, too. The theory compares well with our recent Monte Carlo data on mixtures of L-J and Kihara rod-like molecules.

In applications to real systems the excess thermodynamic functions of binary mixtures were determined (ref. 14). These systems were formerly studied also by Bohn et al. (ref. 10); a comparison of our results with those of Bohn et al. and with experimental data indicates a similar quality of the prediction. In majority of cases the geometric mean value for the unlike parameter,  $\epsilon_{12}$ , should be multiplied by the  $k_{12}$ -factor which is usually  $\approx 0.97$ -1.00. Recently we recalculated the excess properties of some systems with the new parameters of the pure components; as a rule no substantial changes were found. However, in the case of the Xe-C<sub>2</sub>H<sub>6</sub> system better agreement with results of Bohn et al. resulted. In Table 1 a comparison is given of the excess functions of the equimolar Xe-C<sub>2</sub>H<sub>6</sub> system at 161 K calculated from the old and new set of parameters (with  $k_{12} = 1$ ); experimental data and results of Bohn et al. are given, too.

It is obvious from the description of the fitting procedure that the parameters should be used for the description of the equilibria at lower temperatures and/or pressures whereas those given in ref. 12 could better serve at higher temperatures.

#### APPLICATION OF THE PERTURBATION THEORY OF CONVEX MOLECULE FLUIDS TO THE GAUSSIAN OVERLAP SYSTEMS

Systems interacting via the gaussian overlap (GO) pair potential have been studied recently by several authors (see ref. 15 and references given therein). Thermodynamic functions for the GOCE system are given in ref. 15 for three values of  $\lambda$  (the ratio of axes of the ellipsoid of revolution) at several temperatures and densities. The simulation data were interpreted in terms of the Kohler-Fischer theory. There is close resemblance of the gaussian overlap and Kihara potentials following from the fact that in both the potentials the convex shape of molecules is considered and the pair interaction of nonspherical molecules is given by one contribution only. There are important differences: i) In the former potential the energy depends on the mutual orientations of a pair of molecules; ii) there is no hard core, and iii) the mean surface area of two hard GOCE models is not given exactly by the Steiner formula

$$S_{i+j} = S_i + 8\pi R_i R_j + S_j \quad (21)$$

Usually, however, the difference between the simulated values of  $S_{i+j}$  of the GOCE system and those calculated via (21) is small and can be neglected.

Before the application of the convex molecule perturbation theory to the gaussian overlap systems it is necessary to find relationships between the GOCE parameters and those of the Kihara potential. It is essential to put  $\epsilon_K = \epsilon_{\text{GOCE}} = \epsilon_0$ . To relate the  $\sigma$ -parameters we assume equality of the second virial coefficients,

$$B_K(\epsilon, \sigma) = B_{\text{GOCE}}(\epsilon_0, \sigma_0) \quad (22)$$

Whereas the formula for the second virial coefficient of the Kihara molecules is readily available (ref. 16) Kabadi and Steele (ref. 17) listed values of  $\langle (\sigma_{\text{GOCE}}/\sigma_0)^3 \rangle$  of the relationship

$$B_{\text{GOCE}} = -2\pi\sigma_0^3 \langle (\sigma_{\text{GOCE}}/\sigma_0)^3 \rangle \int f_{LJ}(T^*) x^2 dx \quad (23)$$

as a function of the axis ratio of the ellipsoid of revolution. It is evident that the proposed averaging method resembles closely that used in the RAM and other theories.

To formulate the expression for the Helmholtz energy we consider an ellipsoid with the basic

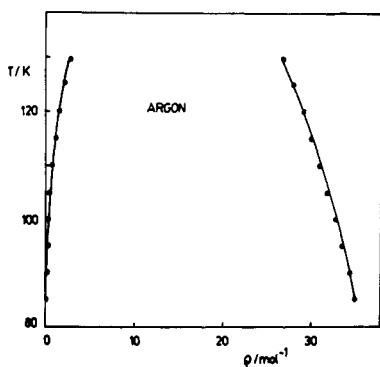


Fig. 1. Coexistence curve of Ar calculated from the convex perturbation theory —; o - experimental data

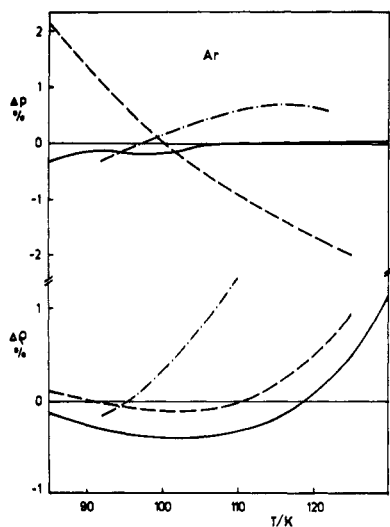


Fig. 2. Per cent deviations in pressure and liquid density; — and - - this work with 3 and 2 adjusted parameters, -.- theory of Kohler and Fischer

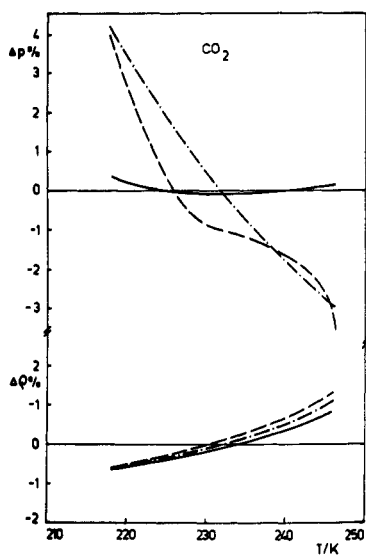


Fig. 3. The same as in Fig. 2

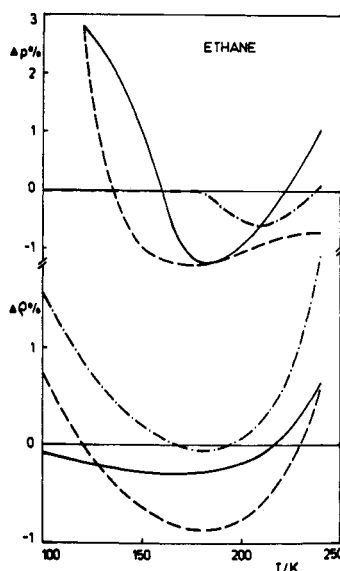


Fig. 4. The same as in Fig. 2.

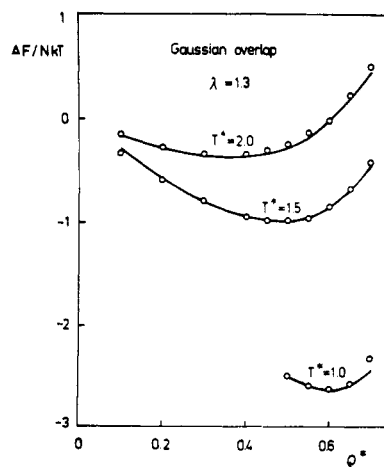


Fig. 5. Helmholtz energy of the gaussian overlap fluid of  $\lambda = 1.3$ ; o - MC data

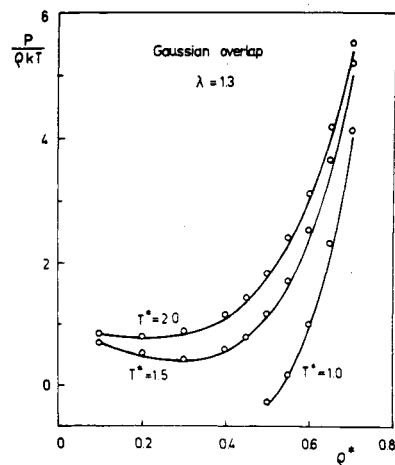


Fig. 6. Compressibility factor of the gaussian overlap fluid of  $\lambda = 1.3$ ; o - MC data

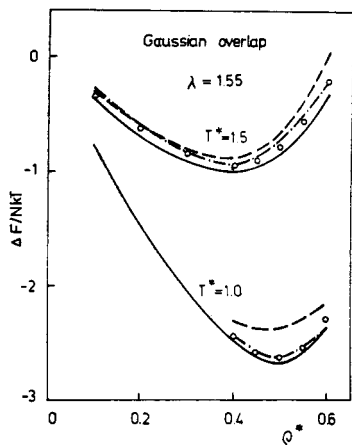


Fig. 7. Helmholtz energy of the gaussian overlap fluid of  $\lambda = 1.55$ , — and - - convex and multicentre perturbation theory -.- multicentre perturbation theory with simulated both the terms

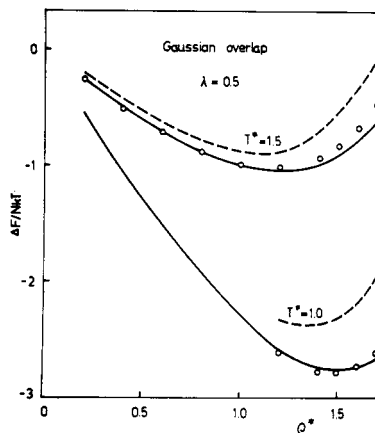


Fig. 8. The same as in Fig. 7 for  $\lambda = 0.5$

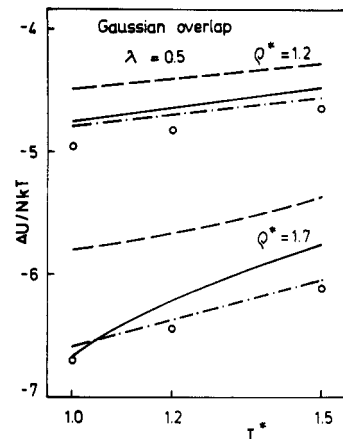


Fig. 9. Residual energy of the gaussian overlap fluid of  $\lambda = 0.5$  at the reduced densities  $\rho^* = 1.2$  and  $\rho^* = 1.7$

axis length,  $\sigma$ , and the length-to-breadth ratio,  $\lambda$ , where both parameters are equal to those of the given GOCE model. We then assume that the mentioned ellipsoid is the parallel body to a hypothetical smaller core with thickness,  $\sigma/2$ , [where  $\sigma$  follows from Eqs (22) and (23)]; the pair potential depends on the surface-to-surface distance,  $s$ , between these two hypothetical cores. If  $d$  is twice the thickness of the representative hard ellipsoid of revolution ( $c = d/\sigma$ ) the geometric characteristics of the representative ellipsoid are

$$R_r = R - \delta, \quad S_r = S - 8\pi R\delta + 4\pi\delta^2, \quad V_r = V - S\delta + 4\pi R\delta^2 - \frac{4}{3}\pi\delta^3 \quad (24)$$

where  $\delta = \sigma(1-c)/2$ . In this way both the reference and perturbation terms can be evaluated from the formerly given relationships. From the study of Sediawan et al. (ref. 15) computer data are available of the GOCE systems with  $\lambda = 0.5, 1.3$  and  $1.55$  at several temperatures and broad range of densities. In Figs 5-6 we present a comparison of our results for the residual Helmholtz energy and pressure for the system with  $\lambda = 1.3$  at the reduced temperatures  $T^* = 1, 1.5$  and  $2$ . In the next two figures (Figs 7-8) a comparison is given of the residual Helmholtz energy calculated from the convex molecule- and multicentre variants of the perturbation theory for more extreme prolate and oblate gaussian overlap models and in Fig. 9 the reduced residual energy is plotted for  $\lambda = 0.5$ . One can see a good agreement of the predicted thermodynamic functions (from the convex molecule version of the perturbation theory) with the simulation data at all conditions even at extreme values of  $\lambda$ . One can thus conclude that i) the simulation data on GOCE systems can be well interpreted by the modified convex-molecule perturbation theory and vice versa the easily obtainable simulation data on GOCE systems can substitute the computer data on convex molecules of the oblate shape ii) the used averaging via the second virial coefficient represents an easy and reliable way of obtaining parameters of the Kihara pair potential.

## HARD BODY EQUATIONS OF STATE AND THEIR MIXING RULES

In majority of perturbation theories the thermodynamic functions of reference systems are evaluated via the properties of the representative hard bodies. Thus, the accurate equation of state is very important for the description of equilibrium behaviour of fluids. For hard spheres the Carnahan-Starling equation has been used most frequently. Recently, however, Kolafa (ref. 18) proposed a modification of it

$$\beta P/\rho = 1/(1-\eta) + 3\eta/(1-\eta)^2 + \eta^2(9-2\eta-2\eta^2)/3(1-\eta)^3 \quad (25)$$

This equation was extended to hs-mixtures and non-spherical bodies by the present author (ref. 19); if  $r = \sum \rho_i R_i$ ,  $q = \sum \rho_i R_i^2$ ,  $s = \sum \rho_i S_i$  and  $v = \sum \rho_i V_i$

$$\beta P/\rho = 1/(1-\eta) + rs/\rho(1-\eta)^2 + qs^2(9-2\eta-2\eta^2)/27\rho(1-\eta)^3 \quad (26)$$

The last relationship with the Boublik-Nezbeda (B-N) rule (ref. 20) to determine parameters  $R_i$ 's is the best available equation of state of mixtures of hard dumbbells and other fused hard-sphere models (FHSM). For pure fluids it reduces to

$$\beta P/\rho = 1/(1-\eta) + 3\alpha\eta/(1-\eta)^2 + \alpha^2\eta^2(9-2\eta-2\eta^2)/3(1-\eta)^3 \quad (27)$$

Another set of accurate equations of state of hard dumbbells has been devised yielding simply tractable expressions for the chemical potential of dumbbells (ref. 19). There are two weak points of the application of Eq. (27) to fused hard-sphere models: i) the B-N rule is not applicable for  $L^* \gg 1$ , ii) with increasing the number of sites of a linear molecule keeping the distance of the outmost sites,  $L$ , constant the FHSMs reduce consequently to the prolate spherocylinder described by the relationship (valid for different types of convex bodies)

$$\beta P/\rho = 1/(1-\eta) + 3\alpha\eta/(1-\eta)^2 + \alpha\eta^2[3\alpha-(6\alpha-5)\eta]/(1-\eta)^3 \tag{28}$$

which for mixtures assumes the form

$$\beta P/\rho = 1/(1-\eta) + r_s/\rho(1-\eta)^2 + [q_s^2(1-2\eta) + 5r_s\eta^2]/3\rho(1-\eta)^3 \tag{29}$$

In passing we note that an analogy of the B-N rule can be employed also with the equation of state of two-dimensional hard dumbbells. We have proposed (ref. 21)

$$\beta P/\rho = 1/(1-\eta_2) + \gamma\eta_2(1+\gamma\eta_2/8)/(1-\eta_2)^2 \tag{30}$$

where  $\gamma = 0_c^2/4\pi A_c$  ( $0_c$  is a perimeter,  $A_c$  - area and  $\eta_2 = \rho A_c$ ). It appears, however, that the B-N rule does not yield accurate enough prediction of the two-dimensional dumbbells; another prescription in which enlarger dumbell is considered for the determination of  $0_c$  and  $A_c$  works more satisfactory.

Several of the hard body expressions combined with an empirical attractive term result in the "augmented van der Waals" (vdW) equations of state. For their applications in routine chemical-engineering methods it is often necessary to employ the one-component equation of state with parameters obtained from the mixing rules. Quite often vdW rule,  $d_m^3 = \sum \sum x_i x_j d_{ij}^3$ , is considered. This, however, is valid only at low densities. To improve the accuracy, the density-dependent mixing rule is introduced. Recently Meyer (ref. 22) proposed

$$d_m^3 = \sum x_i x_j d_{ij}^3 + \frac{3}{4} \eta \sum x_i x_j (d_i - d_j)^2 d_{ij} \tag{31}$$

The introduction of the density dependent mixing rule is, however, not necessary, if we take correctly  $d_m^3 = \sum x_i d_i^3$ , and employ Eq (27) or (28) with  $\alpha$  given by [cf. ref. 23]

$$\alpha_m = \frac{\sum \sum x_i x_j \alpha_{ij} V_{ij}}{\sum x_i V_i} \tag{32}$$

where

$$\alpha_{ij} V_{ij} = \frac{1}{2} [(\alpha_i V_i)^{1/3} (\alpha_j V_j)^{2/3} + (\alpha_i V_i)^{2/3} (\alpha_j V_j)^{1/3}] \tag{33}$$

Even better - and in the case of the hard sphere mixtures the exact results can be found by substituting for  $\alpha^2 \rightarrow \beta_m$  where

$$\beta_m = \frac{[\sum x_i (\alpha_i V_i)^{2/3}]^3}{(\sum x_i V_i)^2} \tag{34}$$

It is evident that mixing rules (32) and (34) are quite simple and lead to the density-independent parameters.  $\beta_m$  differs considerably from  $\alpha_m^2$  only in the case of extreme differences in the size of molecules. For hard sphere mixtures the use of  $\alpha_m$  and  $\beta_m$  corresponds to the application of the exact equation of state. Comparison of the compressibility factors calculated from density-dependent and above-mentioned mixing rules (for  $\alpha_m$  and  $\beta_m$ ) for hard sphere mixtures with the diameter ratios 3:1 and 1:0.6 is disclosed in Figs 10 - 11. In Figs

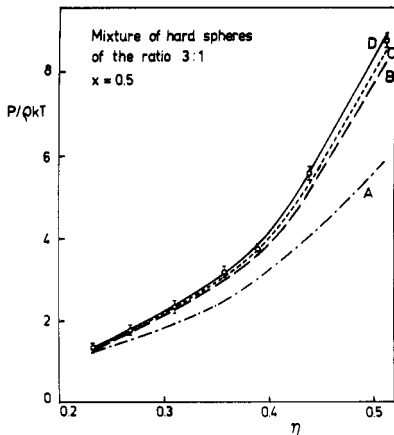


Fig. 10. Compressibility factor of the equimolar hs mixture from A - v.d. Waals rule, B - Eq (32), C - Eq (31), D - Eqs (32), (34)

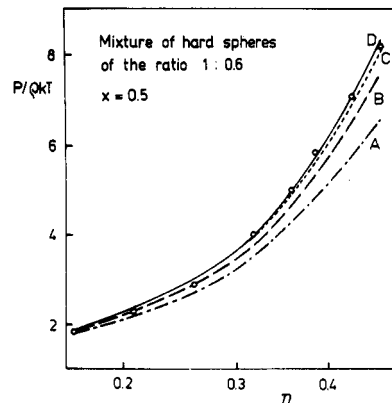


Fig. 11. Compressibility factor of the equimolar hs mixture from A - v.d. Waals rule, B - Eq (32), C - Eq (31), D - Eqs (32), (34)

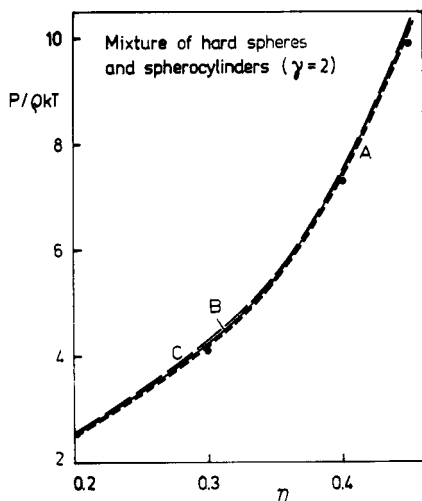


Fig. 12. Compressibility factor of the equimolar mixture of hard spheres-dumbbells ( $L^* = 1$ )  
A - Eq (32), B - exact, C - Eqs (32), (34)

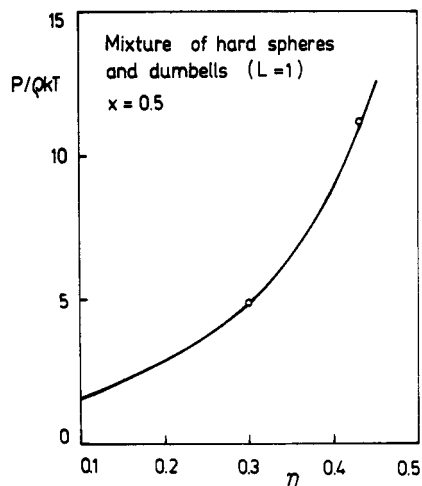


Fig. 13. Compressibility factor of the equimolar mixture of hard spheres-prolate spherocylinders ( $\gamma = 2$ )  
A - Eq (32), B - exact, C - Eqs (32), (34)

12-13 a similar comparison is given for a mixture of spheres and prolate spherocylinders, and for a mixture of hard spheres and hard dumbbells of  $L^* = 1$ . Good accordance was found in the both cases.

It is obvious that the proposed mixing rules yield very good prediction for all the studied systems.

## CONCLUSION

It has been shown how the perturbation theory of convex molecule fluids can be systematically improved while keeping its simple (analytic) form. The theory agrees well with the Monte Carlo data on the L-J and Kihara rod-like fluids and their mixtures and enables a good fit of the coexistence curve of variety of compounds. Theoretical expressions can be easily modified to describe similar models of the interaction employing averaging-to-convex-body technique.

We have presented the equations of state of hard body systems for the different types of hard bodies and simple mixing rules for parameters  $d$ ,  $\alpha$  and  $\beta$  which allow the use of the one-component equation of state to describe the behaviour of mixtures. It has been shown that the better insight into the theory avoids necessity of introducing the density-dependent mixing rules.

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