Molecular fluids and mixtures

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Abstract - On the basis of a WCA-like perturbation
theory various potentials for polyatomic molecules are dis-
cussed. These are multicenter potentials of the Lennard-Jones
and the exp-6-8 type, and also other distributions than site-
site potentials.
For mixtures, the sensitivity of excess properties to the
form of the potential and to shape effects is demonstrated.
Various combining rules are discussed for the calculation of
the potential between unlike partners from pure component
properties.

INTRODUCTION

The approach followed here is that of the perturbation theory. When
the principle correctness is assured by a comparison to computer simulation,
perturbation theory enables quicker and internally more consistent calcula-
tions than any other approach for the high density region. In this way pure
components modelled by one center Lennard-Jones molecules (1CLJ), 2CLJ, 3CLJ,
4CLJ and 6CLJ have been dealt with [1-6], and excess properties of mixtures
of 1CLJ+1CLJ, 1CLJ+2CLJ, 2CLJ+2CLJ, and 1CLJ+4CLJ type have been calculated
[7-10]. On the basis of this experience a short review is given of the
merits and shortcomings of the employed WCA-like perturbation theory (for
short called the Bochum approach), and on the merits and shortcomings of the
multicenter Lennard-Jones potential model. Two directions of modifying this
potential model are discussed: (1) employing a different site-site poten-
tial, (2) using other distributions than site-site potentials in polyatomic
molecules. For mixtures, a discussion of combining rules for the calculating of the
potential between unlike partners from pure component properties follows.

THE STATISTICAL-MECHANICAL CONCEPT

The Bochum approach [1,2] is a WCA-like perturbation theory in the molecular
frame. That means that variables are the center-center distances and the
angles defining mutual orientations of the molecules. Hard fused sphere
bodies are used as reference. The pair distribution function of the repulsive
assembly is calculated via the Baxter method of solving the Ornstein-Zernike
equation with the Percus-Yevick closure. Therefore, the procedure is as fol-
lows:
First, the pair potential is calculated for each mutual orientation of the
two molecules and divided the WCA way at the minimum into a branch of attrac-
tive forces $u^1(r, \omega_1, \omega_2)$ and a branch of repulsive forces $u^\circ(r, \omega_1, \omega_2)$ (where
ω_i is a short notation for the orientation of molecule i). Then the angle
averages $\langle e^{-u^\circ/kT} \rangle$ and $\langle u^1 e^{-u^\circ/kT} \rangle$ are formed. The residual Helmholtz energy
can be written

$$\frac{A^*}{NkT} = \left(\frac{A^*}{NkT}\right)_0 + \frac{\rho}{2} \int \langle g^\circ \frac{u^1}{kT} \rangle \, d\underline{r} , \tag{1}$$

where u^1 and g° are dependent on the mutual orientation. The essential appro-
ximation is now

$$g^\circ = \hat{y} \, e^{-u^\circ/kT} \tag{2}$$

with an angle-independent background correlation function $\hat{y}$. With that, the
perturbation term of eqn. (1) becomes

$$(\rho/2) \int \hat{y} \langle (u^1/kT) \, e^{-u^\circ/kT} \rangle \, d\underline{r} \tag{3}$$

The background correlation function $\hat{y}$ is calculated from the spherically symmetric potential $\hat{u}$ given by

$$e^{-\hat{u}/kT} = \langle e^{-u°/kT} \rangle \quad . \tag{4}$$

Now the only problem left is to lead the Helmholtz energy of the repulsive assembly back to the Helmholtz energy of the hard fused sphere body, which is done by the blip condition

$$\left(\frac{A^*}{NkT}\right)_o = \left(\frac{A^*}{NkT}\right)_H + \frac{\rho}{2} \int \left(\langle e^{-u_H/kT} \rangle - \langle e^{-u°/kT} \rangle\right) \hat{y} \, d\underline{r} \quad , \tag{5}$$

where

$$B = \int \left(\langle e^{-u_H/kT} \rangle - \langle e^{-u°/kT} \rangle\right) \hat{y} \, d\underline{r} \tag{5a}$$

is called the blip integral. Assuming that the centers of the spheres of the hard fused sphere body are identical with the centers of the sites in a multicenter site potential, the blip integral can be adjusted to zero by fixing the proper diameter of the spheres. $(A^*/NkT)_H$ is then calculated from the Boublik-Nezbeda equation [11]. The mean curvature of the hard fused sphere body is calculated from the envelope, volume and surface of more complicated bodies are calculated using the formulae of Lustig [12].

Before quoting the comparisons of the Bochum approach to computer simulation, other approaches with anisotropic references should be mentioned. There is the approach of Boublik and his group [13], which might be termed a perturbation theory in a Kihara frame, as the variable is the shortest distance between a pair of molecular envelopes. The reference here is a hard convex body, and the Kihara frame pair distribution function (which cannot be traced back to a molecular pair distribution function) is given by a semi-empirical extension of the pair distribution function of hard spheres. Another approach [14] uses the site-site frame (with the site-site distance as variable), and calculates the site-site pair distribution function via RISM. For simple linear molecules, the results of the different approaches are about equivalent. Whereas the Kihara frame theory has more potential to deal approximately with more complicated molecules, the molecular frame theory has the best potential for an extension to anisotropic molecules with electric moments. (For almost isotropic molecules with electric moments, cf. the extensive work of Gubbins, Stell at al. [15,16]).

There exist extensive tests of the Bochum perturbation approach by computer simulation. The first concerns the Helmholtz energy of nitrogen at about the triple point [17]. Then the chemical potential of the 2CLJ liquid with an elongation $L = 0.63$ has been compared [18] to applications of the Widom test method [19,20]. The internal energy of 2LCJ liquids agreed very well with computer simulations up to an elongation of $L = 0.505$, but perturbation theory gave 4% too high values at $L = 0.67$ and 7% too high values at $L = 0.793$ [21], which is ascribed to the approximation of using an angle-independent background correlation function. Lustig [22] could receive an almost perfect agreement in the thermodynamic properties of 3CLJ propane, calculated by both perturbation theory and computer simulation. Also, in the pair correlation of 4CLJ CF_4 an excellent agreement was observed [6]. Further comparisons were made by Gupta and Coon [23] for 2CLJ liquids and by Sediawan et al. [24] for the Gaussian overlap model. The agreement was always satisfactory. In the last case the Gaussian overlap potential had to be adjusted to make the blip width sufficiently small.

THE PAIR POTENTIAL

It is very important that the parameters of the pair potential are fitted to the liquid state properties. A fit to the second virial coefficients, e.g., can easily result in big errors in the liquid state properties. The reason is that the characteristic potential parameters are less interrelated for the liquid state properties, where the orthobaric liquid density is mainly determined by the size parameter and the vapour pressure is mainly determined by the energy parameter. An appropriate geometric model (the elongation of an anisotropic molecule) is reflected in the slope of the vapour pressure curve. Most experience is accumulated for the multicenter Lennard-Jones model (nCLJ), which has been remarkably successful in reproducing thermodynamic properties of real liquids in spite of the known shortcomings of the Lennard-Jones potential. The shortcomings are essentially: (1) a too steep repulsion, (2) a too shallow minimum, (3) too negative long range tail. Thermodynamic consequences are: (1) The compressibility factor Z has the tendency to become
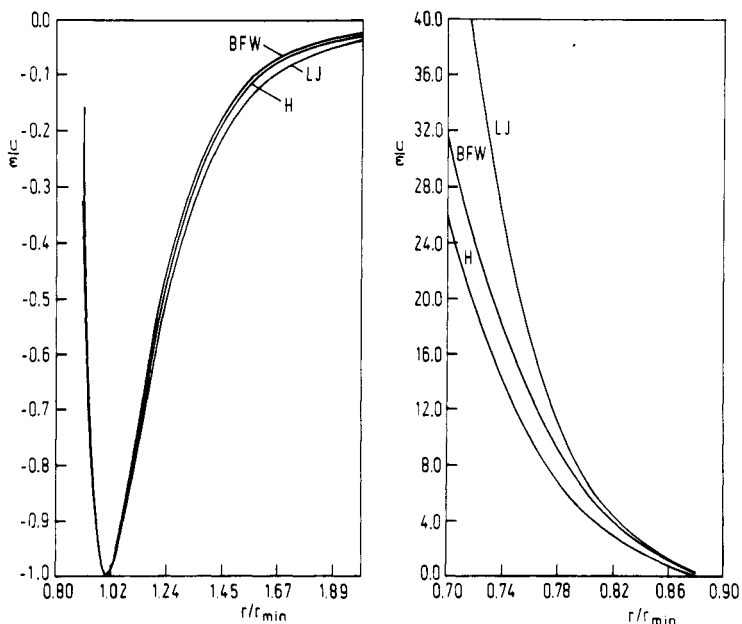
Fig. 1. The H potential in compa-
rison to the LJ and the Barker-
Fisher-Watts potential (BFW)
for argon at medium distances.

Fig. 2. Same as Fig. 1, but
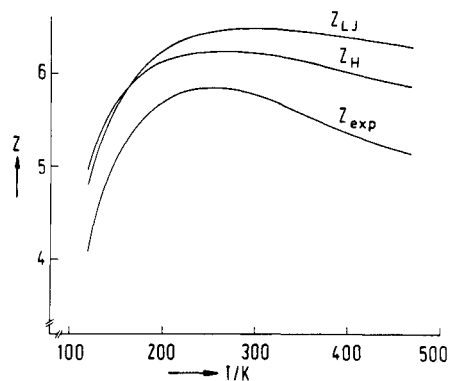at short distances.

Fig. 3. The compressibility
factor Z of methane for the
isochore with $\rho = 30$ mol l^{-1}
as function of temperature, in
comparison to calculations
with the LJ and   H poten-
tial.

too positive at high pressures and temperatures;   (2) The second virial coef-
ficient becomes too positive at low temperatures;   (3) The calculated charac-
teristic energy becomes about twice the ionization potential. The last state-
ment   should   be explained in some detail. According to London [25] , the
dispersion energy is given by

$$u_{disp} = \frac{3}{4} \frac{\alpha^2}{r^6} h\nu ,$$

(6)

where α is the polarizability and $h\nu$ a characteristic energy, which should be
about equal to the ionization potential. As for the Lennard-Jones potential,
the attractive term (given by the dispersion energy) is -2ε (ε being the well
depth)   at the minimum of the pair potential, and as the minimum distance is
$2^{1/6}\sigma$, we have

$$\varepsilon = \frac{3}{16} \frac{\alpha^2}{\sigma^6} h\nu ,$$

(7)

so   that $h\nu$ can be calculated from the potential parameters and the polariza-
bility.
An attempt has been made [26] to construct a two-parameter potential with an
exponential repulsive term and an additional r^{-8} attractive term. In order to
limit the number of parameters to two, the exponent in the repulsive term and
the C_8/C_6 ratio   have   been fixed so as to give good orthobaric properties to
the rare gase liquids. The resulting potential is

$$\frac{u(r)}{\varepsilon} = 374887 \exp(-11.2 \frac{r}{\sigma}) - 2.56314(\frac{\sigma}{r})^6 - 2.56314(\frac{\sigma}{r})^8$$

(8)

Figures 1 and 2 show how this potential - for short called the Hermann (H)
potential - compares to the Lennard-Jones potential and the Barker-Fisher-
Watts potential for argon.

The   improvements   are   shown in Figure 3 for· the compressibility factor of
methane at high temperatures and pressures; in Table 2 for the second virial
coefficients of various substances (with the parameters fitted to the ortho-
baric properties of the liquid and given in Table 1);   and in Table 3 for
the ratio· of the calculated characteristic energy (eqn. 7) to the experimental
ionization potential.

TABLE 1. Pair potential parameters adjusted for a fit of the orthobaric properties of the liquid. The first line gives the reduced elongation $L = l/\sigma$, the second gives $\sigma/\text{Å}$, the third gives $(\varepsilon/k)/K$. For substances with $L = 0$, ε/k is one fourth of the CLJ value.

substance	2CLJ	2CH	SSR-LJ	substance	2CLJ	2CH	SSR-LJ
Ar	0.0	0.0	0.0	CO	0.39	0.39	0.26
	3.4039	3.4003	3.4030		3.2717	3.2862	3.3845
	29.425	31.193	29.434		42.282	44.612	39.657
Kr	0.0	0.0	0.0	F_2	0.505	0.43	0.29
	3.6272	3.6226	3.6325		2.8317	2.9091	3.0181
	41.008	43.473	40.972		53.472	51.350	45.720
CH_4	0.0	0.0	0.0	C_2H_6	0.67	0.67	0.30
	3.7310	3.7243	3.7247		3.5120	3.5208	3.9038
	37.480	39.775	37.524		139.81	149.35	100.927
Xe	0.0	0.0	0.0	Cl_2	0.73	0.73	0.29
	3.9517	3.9475	3.9567		3.2618	3.2727	3.6921
	56.933	60.348	56.867		201.31	215.45	134.428
O_2	0.22	0.22	0.16	C_2H_4	0.74	0.74	0.30
	3.2104	3.2127	3.2604		3.3268	3.3350	3.7590
	38.003	39.990	37.257		137.73	147.35	92.923
N_2	0.3292	0.33	0.22	CO_2	0.793	0.86	0.45
	3.3078	3.3256	3.4072		2.9376	2.9051	3.2308
	36.673	38.61	34.537		161.83	183.93	134.45

TABLE 2. Second virial coefficients B_2/cm^3mol^{-1} for various substances, calculated with the 2CLJ, 2CH, SSR-LJ, and Kihara potential. The parameters are from Table 1 or from Boublik [13].

substance	T/K	exp	2CLJ	2CH	SSR-LJ	Kihara
Ar	81	−276+5	−241	−250.1		
	100	−183.5+1	−167.4	−171.4		
	150	−82.2+1	−81.8	−82.4		
	300	−15.5+0.5	−14.4	−14.5		
	600	+12 +0.5	+12.6	+11.8		
	1000	+22 +1	+21.3	+20.0		
CH_4	110	−330 +10	−285	−293.2		
	150	−182 +3	−166	−168.8		
	200	−105 +2	−99	−99.5		
	300	−41 +1	−41.1	−41.1		
	600	+8.5+1	+7.5	+6.9		
N_2	75	−275 +8	−257	−267	−255	−257.4
	100	−160 +3	−152	−156	−152	−151.4
	150	−71.5+2	−69.7	−70.8	−70.2	−68.0
	200	−35.2+1	−34.9	−35.5	−35.6	−33.1
	300	−4.2+0.5	−4.1	−4.8	−4.9	−2.4
	500	+16.9+0.5	+17.4	+16.1	+16.4	+18.9
	700	+24.0+0.5	+25.3	+23.6	+24.3	+26.7
F_2	80	−240 +40	−229	−236	−228	−231.1
	100	−156 +10	−150	−153	−149	−150.0
	150	−70.9	−68.7	−69.5	−69.1	−67.3
	200	−37.6	−36.1	−36.8	−36.8	−34.4
	250	−20	−18.7	−19.4	−19.6	−16.9
	300	−9.5	−8.0	−8.8	−8.9	−6.1
C_2H_4	198.77	−315	−314	−327	−294	−289.3
	223.22	−251	−250	−258	−237	−232.8
	250	−201 +2	−200	−205	−191	−187.8
	300	−138 +1	−137.4	−140.3	−134	−131.1
	350	−99 +1	−97.7	−99.3	−96.8	−94.3
	450	−51.7+1	−50.0	−50.8	−52.0	−49.6
C_2H_6	200	−410 +10	−400	−418	−381	−375.5
	260	−243 +2	−240	−246	−232	−228.6
	300	−182 +2	−180	−184	−176	−173.0
	400	−96.0+1	−96.3	−97.6	−96.0	−93.2
	600	−24.5+0.5	−25.3	−25.9	−27.7	−25.0

TABLE 3. The ratio of the characteristic energy to the experimental ioni-
zation potential, hν/I, for various potential models. The parameters
are from TAble 1 or from Boublik [13].

substance	2CLJ	2CH	SSR-LJ	Kihara	substance	2CLJ	2CH	SSR-LJ	Kihara
Ar	2.01	1.36	2.01	2.01	N_2	1.87	1.30	2.10	1.23
Kr	1.98	1.34	1.98	1.98	CO	1.79	1.24	2.06	1.07
CH_4	2.19	1.47	2.19	2.19	C_2H_6	2.10	1.46	2.86	1.34
Xe	2.03	1.38	2.03	2.03	C_2H_4	1.80	1.25	2.53	1.28
O_2	2.48	1.68	2.67	1.40	CO_2	1.96	1.35	2.90	0.82

Another question concerns the pair potential of polyatomic mole-
cules. At present, there are three different suggestions. The most anisotro-
pic choice is the Kihara potential, then comes the site-site potential, and
the least anisotropic is Lucas' SSR-MPA potential [27], where only the re-
pulsive term is distributed to the sites, whereas the attractive term origi-
nates from the molecular center. We will make a systematic comparison on the
basis .of the Lennard-Jones potential acting either between the nearest molecular
distances, or between the sites, or with the attractive term between molecular
centers. The anisotropy of the dispersion energy, taken into account by Lucas
[27], is neglected here.This simplified potential should be called SSR-LJ. As
for this potential no parameters are available which are fitted to the ortho-
baric properties of the liquid, we have determined them on the basis of our
perturbation theory with a hard dumbbell reference. These parameters are
compared in Table 1 to the 2CLJ-parameters. It is seen that the elongations
are systematically smaller, which is compensated by a bigger size parameter
σ. Figure 4 shows for ethane the potential behaviour for four significant
orientations, with the parameters from Table 1 or from Boublik [13], resp..
Figure 5 compares the center-center pair distribution function for the three
potentials.
Another significant difference is the ratio of characteristic energy to
ionization potential, which is more or less constant for 2CLJ, increases
with elongation for SSR-LJ, but decreases with elongation for the Kihara
potential. These numbers are given in Table 3. The second virial coeffi-
cients, calculated with the potential parameters from the liquid phase proper-
ties, are added in Table 2. It seems premature to draw definite conclusions
from these comparisons, but at present it can be said that the nCLJ-
(or nCH-) potential offers a very reasonable model.
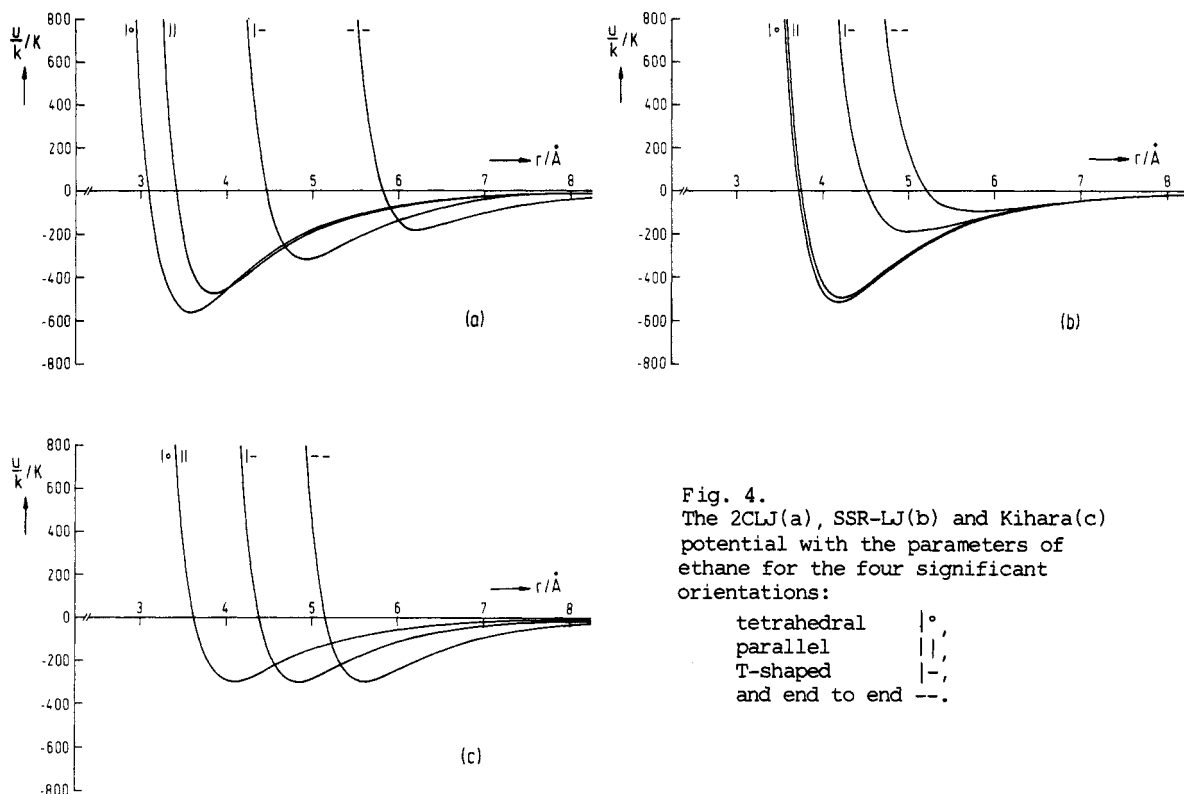

(a)

(b)

(c)

Fig. 4.
The 2CLJ(a), SSR-LJ(b) and Kihara(c)
potential with the parameters of
ethane for the four significant
orientations:

tetrahedral |°,
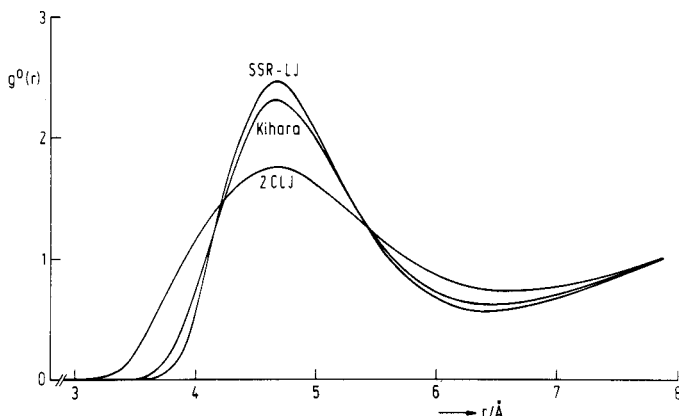parallel ||,
T-shaped |-,
and end to end --.

Fig.5. The center-center pair distribution function for ethane for the 2CLJ, SSR-LJ, and Kihara potential.

EXTENSION TO MIXTURES

The straightforward extension of eqn. (1), (3), (5) to mixtures yields

$$\left(\frac{A^*}{NkT}\right)_{mi} = \left(\frac{A^*}{NkT}\right)_{o,mi} + \frac{\rho}{2} \Sigma \; x_i x_j \int \hat{y}_{ij} <(u_{ij}/kT)e^{-u^o_{ij}/kT}>d\underline{r} \tag{9}$$

and

$$\left(\frac{A^*}{NkT}\right)_{o,mi} = \left(\frac{A^*}{NkT}\right)_{H,mi} + \frac{\rho}{2} \underset{i,j}{\Sigma} x_i x_j \; B_{ij} \tag{10}$$

where the x_i are mole fractions of component i.
The evaluation of $\hat{y}_{ij}$ via Baxter's method has been done in an approximate way by Perram [28] and in a refined version by Fischer and Lago [7]. The question remains how to deal with the sum of the blip integrals in eqn. (10). Fischer and Lago retained the condition for the pure components $B_{ii} = 0$ and $B_{jj} = 0$, and evaluated the term with B_{ij} as a correction term, whereby $<e^{-u^H_{ij}/kT}>$ was given by the condition of additivity of sphere diameters

$$d_{ij} = (d_{ii} + d_{jj})/2 \tag{11}$$

Later, following a suggestion by Perram, Bohn et al. [8] used

$$x_1 \; B_{11} + x_2 \; B_{12} = 0$$

$$x_1 \; B_{12} + x_2 \; B_{22} = 0 \tag{12}$$

together with eqn. (11) for determining d_{11}, d_{12}, and d_{22} in the mixture. This way d_{ij} became slightly dependent on composition. However, comparison with computer simulaiton showed the advantage of this procedure. Recently, Shukla [29] has used the same conditions.
Again, several comparisons to computer simulation have been made. First, it was possible [30] to reproduce the extensive Monte Carlo calculations of Singer and Singer [31] on model mixtures of spherical molecules. Then, Haile [32] has compared g^E for repulsive soft spheres and Coon et al. [33] have compared excess properties for 1CLJ+2CLJ mixtures. Finally, Lotfi, Lotfi and Fischer [34] have calculated Henry constants for mixtures of spherical molecules by the perturbation theory and by computer simulation. Even in these extreme cases the agreement was very satisfactory.

Two questions should be answered now on the basis of the perturbation theory. First, how sensitive are the excess properties of mixtures of spherical molecules on the pair potential used? Second, how important are shape effects for excess properties?
In dealing with these questions, the model mixtures of Singer and Singer [31] are used as the start. That means that the calculations are for zero pressure, for T = 97 K, for $\varepsilon_{12}/k=133.5$ K, and for $\sigma_{12} = 3.596$ A. Assuming the Lorentz-Berthelot conditions, i.e.

$$\varepsilon_{12} = \sqrt{\varepsilon_{11} \varepsilon_{22}} \tag{13a}$$

and

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \quad , \tag{13b}$$

the excess properties will be calculated as a function of the energy ratio

$$\delta = (\varepsilon_{22}/\varepsilon_{12} - 1)\sqrt{\varepsilon_{12}/\varepsilon_{22}} \tag{14}$$

and size ratio
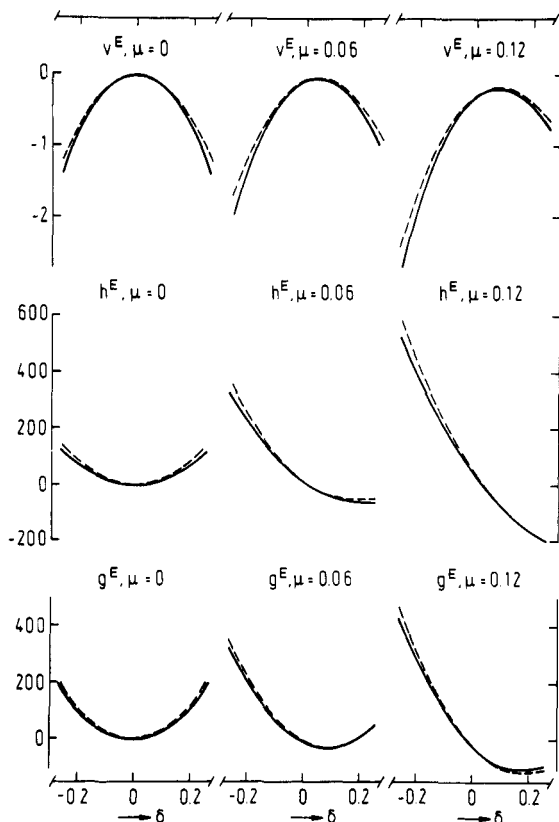
$$\mu = \sigma_{22}/\sigma_{12} - 1 \quad . \tag{15}$$

TABLE 4. The increment in excess Gibbs energy, $g^E/J \ mol^{-1}$, when molecule 2 is elongated from $L = 0$ to $L = 0.793$. The model mixture is that of Singer and Singer
($p = 0$, $T = 97$ K, $\varepsilon_{12}/k = 133.5$ K, $\sigma_{12} = 3.596$ Å).

δ \ μ	0	0.06	0.12
–0.211	–161	–45	+71
0	–138	–28	+86
+0.211	–115	– 6	+102

Fig.6. The excess properties for the Singer and Singer model mixtures for 1CLJ and 1CH potentials.

Figure 6 shows this behaviour for mixtures of 1CLJ molecules (dashed) and 1CH molecules (full). The differences are small, except for extreme cases of δ. The H-potential is much more softly repulsive, which results in slightly more negative v^E values, and in turn in slightly less positive g^E and h^E values.

In order to answer the second question, we first model molecule 1 and molecule 2 as 1CLJ (with the parameters fitted to vapour pressure and orthobaric density). Then we elongate molecule 2 (again with 2CLJ-parameters which satisfy vapour pressure and density). The difference in g^E, which results from this elongation, is given in Table 4 as a function of the 1CLJ energy and size ratios.
It is seen that the elongation leads to a negative increment in g^E, when we start from equally sized spheres, i.e. when σ_{22} becomes smaller than σ_{11} in the elongation process. But when we start from a small sphere 1 and a big sphere 2 (μ big), then the elongation process leads to more equally sized σ_{11} and σ_{22}, and the increment in g^E becomes positive.
The dashed lines of Figure 6 and Table 4 are part of our general correlation formulae for the excess properties of 1CLJ+2CLJ mixtures [9].

COMBINING RULES

It is a crucial problem in the treatment of mixtures to assign the unlike interaction parameters ε_{12} and σ_{12}, in other words, to determine the small deviations from the Lorentz-Berthelot rule, characterized by the parameters ξ and η:

$$\varepsilon_{12} = \xi\sqrt{\varepsilon_{11} \ \varepsilon_{22}} \qquad (16a)$$

$$\sigma_{12} = \eta(\sigma_{11} + \sigma_{22})/2 \qquad (16b)$$

For the long range tail of the potentials, the use of the simplified London formulae for the dispersion energy [35] is now well established, with the characteristic energies calculated via eqn. (7). This leads to

$$\varepsilon_{12} \ \sigma_{12}^6 = (3/8)\alpha_1\alpha_2 \ h\nu_1 \ h\nu_2/(h\nu_1 + h\nu_2) \qquad (17)$$

For n_1CLJ + n_2CLJ mixtures the factor $n_1 n_2$ has to be added on the left hand side. If σ_{12} is assumed to be the arithmetic mean (i.e. $\eta = 1$), this leads to

$$\xi = \left[\frac{\sqrt{\sigma_{11} \sigma_{22}}}{(\sigma_{11}+\sigma_{22})/2} \right]^6 \frac{\sqrt{h\nu_1 h\nu_2}}{(h\nu_1+h\nu_2)/2} \tag{18}$$

That means, ξ is given by the ratio of the geometric to arithmetic mean of the σ's to the sixth power times this ratio for the $h\nu$'s to the first power. It is, therefore, very important to have reliable σ and $h\nu$ values for making predictions of the unlike interaction. As it has been shown, this depends very much on choosing the correct molecular model.
The assumption $\eta = 1$, on which eqn. (18) is based, has been termed later [8] the old method of Kohler (KO). It is quite a difficult problem to arrive at better values. Kohler et al. [36] thought that it is the effective hard diameter, which is responsible for the repulsive forces, and assumed additivity for it. In order to have a simpler relation than the blip, they used the BH1 prescription [37], which can be formulated generally for nCLJ as

$$\int (<e^{-u_H/kT}> - <e^{-u_o/kT}>)dr = 0 \quad , \tag{19}$$

where $<e^{-u_H/kT}>$ depends on the hard diameter d. The new relation

$$d_{12} = (d_{11} + d_{22})/2 \tag{20}$$

requires an iterative solution, which is easily obtained. Note that the integrand in eqn. (19) differs from the integrand in the blip (eqn. 5a) only by the factor $\hat{y}r^2$, so that the new procedure comes very near to choosing a σ_{12}, which leads together with conditions (12) to zero blips $B_{12} = B_{11} = B_{22} = 0$. It gives mostly η values slightly larger than unity. It has been termed [8] the new method of Kohler (KN), or the new extended method (KNE), when applied to multicenter Lennard-Jones mixtures.
Recently [27], another method for determining η has been recommended, which goes back to the work of Smith [38] and Kong [39]. Their principal assumption can be rewritten as

$$\left(\frac{du_{12}^{rep}}{dr}\right)_{r_1+r_2} = \left(\frac{du_{11}^{rep}}{dr}\right)_{2r_1} = \left(\frac{du_{22}^{rep}}{dr}\right)_{2r_2} \quad , \tag{21}$$

which means that the repulsive force exerted by one molecule for a certain deformation is independent of the nature of the colliding molecule. Though one might question this assumption, the main drawback in the further treatment was the insertion of the r^{-12} part of the LJ-potential in u^{rep}. This leads immediately to

$$\varepsilon_{12}\sigma_{12}^{12} = \{[(\varepsilon_{11}\sigma_{11}^{12})^{1/13} + (\varepsilon_{22}\sigma_{22}^{12})^{1/13}]/2\}^{13} \quad , \tag{22}$$

which together with eqn. (17) gives ε_{12} and σ_{12}, or ξ and η (this combination might be termed Kohler-Smith-Kong (KSK).
The repulsive potential which is thought to be responsible for the structure is not the r^{-12} part of the LJ-potential, but that part originating from the WCA-division of the potential, i.e.

$$u^{rep} = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] + \varepsilon \qquad r < 2^{1/6}\sigma \tag{23}$$

However, for this potential the condition (21) does not lead to a simple formula like eqn. (22), but gives η values depending on the assumed colliding distance r_1+r_2. For colliding distances slightly smaller than σ_{12} the η values are of the same order as with the KN rule.
The inconsistency in the repulsive potential used in the KSK rule with that used in the statistical mechanical concept would eliminate the KSK rule if it would not give sometimes relatively good results. For this reason we will discuss it further. It seems to be a fact that the KO or KN rule has a tendency to produce somewhat high ξ values. The use of the very softly repulsive r^{-12} term of the LJ-potential in the Smith-Kong treatment leads to a relatively big η value, which in turn brings the ξ value down. However, when an independent check on ξ and η is possible, the general finding is that the KSK ξ is quite good but the KSK η is too large. This is illustrated in Figure 7 for the example of the Kr+Xe mixture, which shows what pairs of ξ and η would be demanded to reproduce the excess properties v^E, g^E, and h^E. It is seen that h^E and g^E determine essentially ξ, but v^E is also very strongly

η-dependent. In that example, the KSK-rule gives a slightly too small ξ, whereas the KN-rule is on the high side. But the η value produced by KSK is definitely too large.

There is another difficulty with the KSK rule for n_1CLJ + n_2CLJ mixtures. For very small elongations, the rule should go continuously over to the 1LCJ+1CLJ mixture, eqn. (22). Then it should be written

$$n_1 n_2 \varepsilon_{12} \sigma_{12}^{12} = \{[(n^2_1 \varepsilon_{11} \sigma_{11}^{12})^{1/13} + (n^2_2 \varepsilon_{22} \sigma_{22}^{12})^{1/13}]/2\}^{13} . \qquad (24)$$

This we will call KSKI. For large elongations, where only different sites "see" each other, formula (22) should be retained, but with the ε_{ij} and σ_{ij} being the site-site potential parameters. This version we call KSKII.[1] Table 5 gives a summary of various systems calculated by KNE, KSKI, and KSKII.
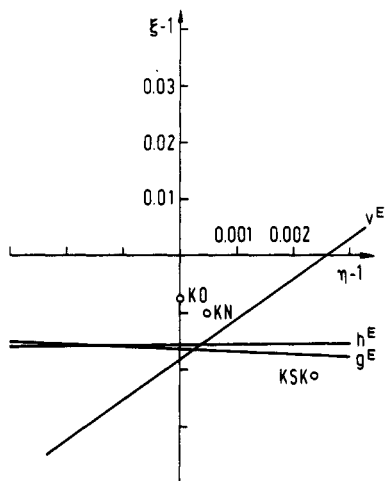

Fig. 7. The values of ξ and η needed to reproduce the excess properties of Kr + Xe, and the prediction by various combining rules.

TABLE 5. Comparison of experimental and predicted excess properties $g^E/J\ mol^{-1}$, $h^E/J\ mol^{-1}$, and $v^E/cm^3 mol^{-1}$ of 1CLJ+2CLJ and 2CLJ+2CLJ mixtures.

			exp	KNE	KSKI	KSKII
Ar + O_2		g^E	37	10	−1.6	82
84 K		h^E	60	16	−11	121
		v^E	0.14	0.01	−0.03	0.30
Ar + N_2		g^E	34	35	30	82
84 K		h^E	51	34	27	112
		v^E	−0.18	−0.15	−0.18	0.11
Ar + CO		g^E	57	43	46	99
84 K		h^E	96	53	59	146
		v^E	0.09	−0.02	−0.01	0.28
CH_4 + N_2		g^E	170	106	97	253
91 K		h^E	138	57	44	297
		v^E	−0.54	−0.57	−0.63	0.20
Kr + C_2H_4		g^E	240	136	146	212
116 K		h^E	315	154	144	239
		v^E	0.21	−0.13	−0.17	0.01
Xe + C_2H_4		g^E	145	108	14	275
161 K		h^E	185	131	−14	399
		v^E	0.35	0.07	−0.27	0.63
Ar + C_2H_6		g^E	317	191	422	272
91 K		h^E	239	127	439	232
		v^E	−0.38	−0.75	−0.17	−0.54
Kr + C_2H_6		g^E	80	26	79	56
116 K		h^E	49	−14	65	33
		v^E	−0.22	−0.34	−0.20	−0.26
CH_4+C_2H_6		g^E	121	109	125	141
104 K		h^E	74	59	85	106
		v^E	−0.45	−0.59	−0.54	−0.50
Xe + C_2H_6		g^E	−29	3	−91	92
161 K		h^E	−52	−19	−172	109
		v^E	−0.12	−0.10	−0.41	0.18
O_2 + N_2		g^E	40	55	57	81
78 K		h^E	60	59	62	100
		v^E	−0.25	−0.21	−0.20	−0.09
N_2 + CO		g^E	23	8	14	53
84 K		h^E	−	11	23	91
		v^E	0.13	0.01	0.05	0.32
C_2H_4+C_2H_6		g^E	99	69	109	113
161 K		h^E	193	100	162	169
		v^E	0.16	0.10	0.23	0.25

We believe that inspite of some shortcomings the KNE rule should be preferred, and that the inconsistency inherent in the KSK rule masks some approximations of the models, which could be easier seen and eventually remedied otherwise.

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