

General Form of the Cross-Energy Parameter of Equations of State

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Phase equilibrium calculations with cubic equations of state are sensitive to mixing and combining rules employed. In this work, we present a suitable general form of the combining rule for the cross-energy parameter, often considered to be the key property in phase equilibrium calculations. The proposed rule is derived from molecular considerations, namely, the London–Mie theory. The typically used geometric mean (GM) and other combining rules can be deduced from this expression from different values of the parameter n , which is the attractive tail of the Mie potential. We show that using this n parameter as the variable instead of the commonly employed k_{ij} offers useful insight into the behavior of cubic equations of state for a large number of asymmetric systems including gas/alkanes, polymer solutions and blends, and alcohol/alkane and gas/solid systems.

1. Introduction

The mixing and combining rules of the fluid parameters play a crucial role in the performance of equations of state (EoS). Various choices have been proposed for both the size-related co-volume (b) and the energy (a) parameters. Over the years, the classical van der Waals one-fluid mixing rules have found widespread use, especially when combined with the geometric mean (GM) rule for a_{12} and the arithmetic mean (AM) rule for b_{12} . This choice seems justified also from a theoretical point of view, as shown in a recent publication.¹

In particular and as shown from the analysis by Kontogeorgis et al.¹ and Harismiadis et al.,² the use of the AM rule for b_{12} is quite justified in cubic equations of state of the vdW type, that is, those using the vdW repulsive term. Using this rule for b_{12} , the repulsive term of the equation resembles functionally that of well-known and successful activity coefficient models for asymmetric systems, for example, Flory–Huggins and entropic-FV.³ This statement indicates that the cubic equations of state can be valid for both symmetric and size-asymmetric systems, at least from this respect. As shown,¹ the AM rule for b_{12} performs, when used in cubic EoS, much better compared to other alternatives including the Lorentz rule, which is equivalent to the AM rule of the molecular diameters. The Lorentz rule is often employed in molecular simulations.

The situation is far less clear for the GM combining rule typically used for the energy parameter ($\alpha_{12} = \sqrt{\alpha_1\alpha_2}$) and it is not surprising that most efforts in improving the mixing/combining rules of equations of state focus on the energy term and parameters. Indeed, in the theoretical analysis mentioned,¹ it is shown that the GM rule progressively deteriorates for highly size-asymmetric systems, though it is valid for medium asymmetric ones. It seems that a more general com-

binning rule for the cross-energy parameter, which will incorporate size effects as well, could be more suitable for covering greater asymmetric ranges.

The purpose of this work is to provide an analysis of the GM combining rule for the cross-energy parameter of cubic equations of state. In particular, the aim is to investigate the validity of this combining rule for both symmetric and asymmetric systems. The term asymmetric implies in this discussion systems with either size differences (e.g., gas/alkanes) or energy differences (e.g., gas/solids and alcohol/alkanes). Toward this objective, a generalized formula for the combining rule (of which the GM and other combining rules are special cases) will be derived and studied. The starting point for deriving this formula will be the London theory for dispersion forces and the Mie equation for the intermolecular potential.

2. General Combining Rule for the Energy Parameter

The starting point for the derivation of the rule is the London equation for the cross-attractive intermolecular potential (Γ_{12})

$$\Gamma_{12} = \sqrt{\Gamma_1\Gamma_2} \left(\frac{2\sqrt{I_1I_2}}{I_1 + I_2} \right) \quad (1)$$

and the Mie potential function

$$\Gamma_{12} = \frac{m}{m-n} \left(\frac{m}{n} \right)^{n/(m-n)} \epsilon_{12} \left[\left(\frac{\sigma_{12}}{r} \right)^m - \left(\frac{\sigma_{12}}{r} \right)^n \right] \quad (2)$$

where I_i is the ionization potential of component i , ϵ_{12} is the molecular cross-energy parameter, σ_{12} is the molecular cross diameter, and r is the distance of the molecules.

Equation 1 is strictly valid for molecules, which exhibit only dispersion forces, but its practical validity is considered to be greater. Inserting the attractive part of eq 2 into eq 1, we get

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$$\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2} \left(\frac{\sqrt{\sigma_1 \sigma_2}}{\sigma_{12}} \right)^n \left(\frac{2\sqrt{I_1 I_2}}{I_1 + I_2} \right) \quad (3)$$

A similar equation had been first proposed by Hudson and McCoubrey⁴ and later by numerous researchers.

Equation 3 is the general energy combining rule in terms of the molecular energy (ϵ) and size (σ) parameters. The exponent n is a characteristic of the potential function. The ionization potential term is often ignored. However, as shown for CO₂/alkanes by Coutinho et al.,⁵ the ionization term can be approximated using the co-volume parameters:

$$I \propto \frac{1}{\sigma^3} \Rightarrow \frac{2\sqrt{I_1 I_2}}{I_1 + I_2} \cong \left(\frac{\sqrt{b_1 b_2}}{b_{12}} \right)^{-1} \quad (4)$$

Equation 4 is not restricted to CO₂ systems but holds for other gas/alkane systems as well (CO, methane, ethane, hydrogen sulfide, etc.) and can thus be considered a reasonable approximation for the needs of this study. The linear plot of the ionization potential with $1/\sigma^3$, which forms the basis for eq 4, is shown graphically in Figure 1.

Using the following basic proportionalities—relations between “microscopic” (ϵ , σ) and “macroscopic” properties (T_c , V_c , a , b)

$$\epsilon \propto \frac{a}{b} \propto T_c$$

$$\sigma^3 \propto b \propto V_c$$

and upon combining eqs 3 and 4, we arrive at the expressions for the cross-energy parameters, the cross-critical temperature (T_{c12}),

$$T_{c12} = \sqrt{T_{c1} T_{c2}} \left(\frac{\sqrt{V_{c1} V_{c2}}}{V_{c12}} \right)^{(n/3)-1} \quad (5)$$

and the cross-energy parameter of cubic equations of state (α_{12}):

$$\alpha_{12} = \sqrt{\alpha_1 \alpha_2} \left(\frac{\sqrt{b_1 b_2}}{b_{12}} \right)^{(n/3)-2} \quad (6)$$

Using eqs 5 and 6, the following simple expressions can be derived for the interaction parameter k_{12} (correction from the GM rule for the cross-critical temperature $T_{c12} = \sqrt{T_{c1} T_{c2}}(1 - k_{12})$ and the cross-energy parameter $\alpha_{12} = \sqrt{\alpha_1 \alpha_2}(1 - k_{12})$)

$$k_{12} = 1 - \left(\frac{\sqrt{b_1 b_2}}{b_{12}} \right)^{(n/3)-2} \quad (7a)$$

or

$$k_{12} = 1 - \left(\frac{\sqrt{V_{c1} V_{c2}}}{V_{c12}} \right)^{(n/3)-1} \quad (7b)$$

Using this analysis, various combining rules previously proposed in the literature can be deduced from different values for the exponent n of this general equation, as shown in Table 1.

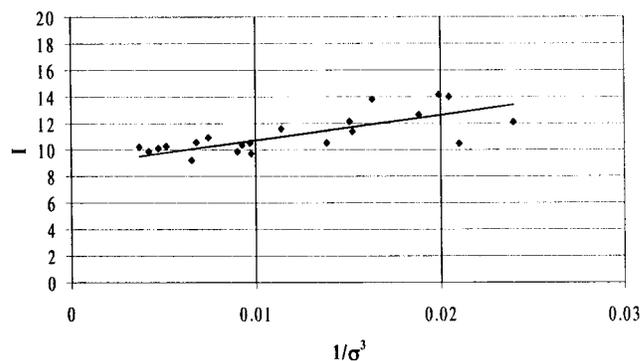


Figure 1. Plot of the ionization potential as a function of the quantity $1/\sigma^3$ where σ is the molecular diameter. The database includes a variety of gases and hydrocarbons.

As can be seen in Table 1, the classical GM rule for α_{12} is derived from the generalized formula for $n = 6$, which is the value that corresponds to the widely used Lennard-Jones potential function. This is an interesting result and offers some theoretical support for the GM rule. If the ionization potential term is ignored, as is usually done in the literature, then the GM rule is derived for $n = 3$; on the basis of this result, it is often stated in the literature that the GM rule is of an empirical nature. In this work, a different light is given in this perspective. Moreover, the Berthelot rule, as employed in simulation studies, is obtained for $n = 3$.

3. Results and Discussion

The list of investigated systems is given in Table 2. In the same table is also provided information on the type of experimental data (vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE), Henry’s law constants and solid–gas equilibrium data (SGE)), the equation of state used, and the reference from which the binary interaction parameters have been obtained. Interaction parameters employed have been obtained with four different equations of state, three cubic ones (van der Waals, Soave–Redlich–Kwong (SRK), and Peng–Robinson (PR)) and a noncubic one (cubic-plus-association (CPA)).

All LLE data correspond to UCST-type phase equilibrium curves. For alcohol/alkane systems, the CPA equation of state proposed by Kontogeorgis et al.¹⁰ is employed. CPA is a noncubic equation of state, given as a sum of SRK and a separate term accounting for the hydrogen-bonding effects. The hydrogen-bonding term of CPA is the same as that in the well-known statistical association fluid theory (SAFT). CPA has been shown to be very successful for multicomponent alcohol–water–hydrocarbon systems.¹¹ Thus, because the association effects are properly accounted for, it can be stated that the physical term of CPA should behave similarly to cubic equations of state.

The aim of this work has been to investigate and compare the trend of the exponent n of eqs 6 or 7a against the size asymmetry with the trend of the typically employed k_{ij} interaction parameter (correction to the GM rule for energy).

For most of the systems studied such as CO₂, methane, and hydrogen sulfide with n -alkanes, experimental data were available over a large asymmetry (up to nC_{44}) and temperature range, thus allowing us to include both of these factors (size and temperature) into our analysis.

Table 1. Exponent Values Corresponding to Literature Combining Rules

<i>n</i> value	rule	comments
6	the classical geometric mean rule $\sqrt{\alpha_1\alpha_2}$	typically used <i>n</i> = 6 is the Lennard-Jones fluid
3	the Berthelot rule $\epsilon_{12} = \sqrt{\epsilon_1\epsilon_2} \Rightarrow$ $\alpha_{12} = \sqrt{\alpha_1\alpha_2} \left(\frac{\sqrt{b_1b_2}}{b_{12}} \right)^{-1}$	often employed in simulations valid for polymer solutions ²
5.25	Radosz and co-workers ⁶	hydrogen, methane, CO ₂ /hydrocarbons
7.5	Lee and co-workers ⁷	alkane solutions (C ₁ –C ₁₀)
7.2	Trebble and Sigmund ⁸	CO ₂ /hydrocarbons
6.75	Vidal and co-workers	
3.75	Plocker and co-workers ⁹	hydrogen, CO ₂ , H ₂ S/hydrocarbons

Table 2. Systems Studied in This Work

system	type of equilibria	EoS	experimental source
methane/alkanes	VLE	PR	12
	Henry	vdW	13
ethane/alkanes	VLE	PR	1
	Henry	vdW	13
propane/alkanes	VLE	PR	1
	Henry	vdW	13
butane, hexane/alkanes	VLE	PR	1
	Henry	vdW	13
Ar, Kr, Xe/alkanes	Henry	vdW	13
CO ₂ /alkanes	VLE	PR	14
	Henry	vdW	13
CO/alkanes	Henry	vdW	13
N ₂ /alkanes	VLE	PR	15
	Henry	vdW	13
H ₂ S/alkanes	VLE	PR	16
	Henry	vdW	13
polymer solutions	VLE and LLE (UCST)	vdW	17,2
		SRK	18
polymer blends	LLE(UCST)	vdW	19
CO ₂ /solids	SGE	PR	20
alcohol/alkanes	VLE and LLE (UCST)	CPA	21,22

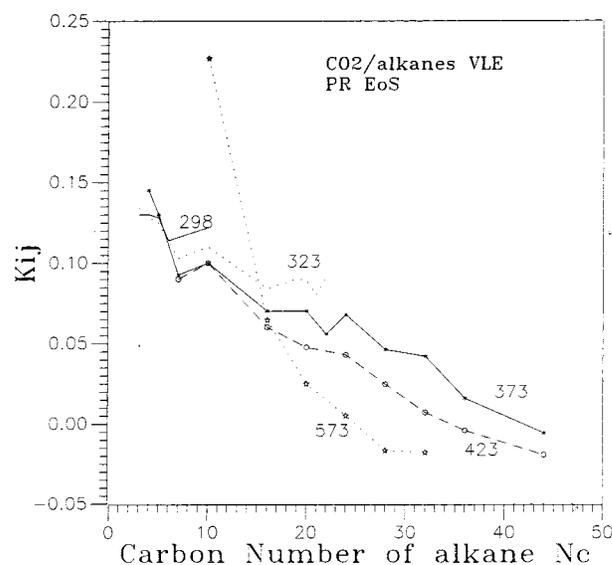
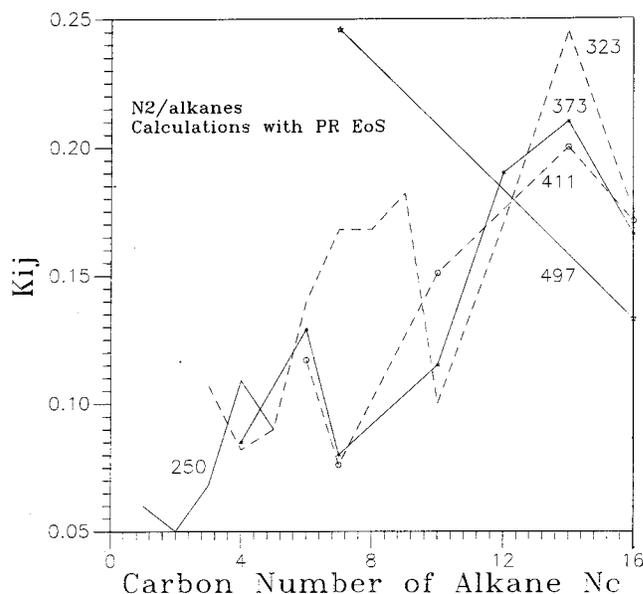
The estimation of the exponent *n* has been based on the reported values of the *k_{ij}* interaction parameters and the co-volume parameters using eqs 6 or 7a. Critical properties of heavy *n*-alkanes are obtained from recent experimental measurements²³ or adequate correlations^{24–26} and those of polymers from the original publications.^{2,17–19}

For brevity, only results for some of the most characteristic systems studied are presented graphically in Figures 2–13.

The following points summarize our observations:

1. As known, *k_{ij}* is a function of both temperature and the system's asymmetry. Except at very low asymmetries and temperatures, *k_{ij}* usually decreases with increasing chain length difference, as can be seen in Figure 2 for CO₂/alkanes. The same behavior is observed in many other gas/alkane systems, for example, ethane, propane, CO, and hydrogen sulfide. The temperature dependency has typically a U-type form, as verified by many researchers.^{5,12,14,15} Because our aim is to investigate the chain length effect of the interaction parameter, in most plots results are presented at various isotherms.

2. The behavior of methane/alkanes and nitrogen/alkanes is quite interesting. Particularly for nitrogen/alkanes, where data are available only up to *n*C₁₆, *k_{ij}* systematically increases with chain length, as can be seen in Figure 3. The same holds for methane/alkanes up to *n*C₁₆ and it subsequently decreases (Figure 4). The decrease of *k_{ij}* with chain length is more pronounced at higher asymmetries and/or temperatures.

**Figure 2.** Plot of *k_{ij}* with alkane carbon number for CO₂/alkanes at various temperatures using the Peng–Robinson equation of state.**Figure 3.** Plot of *k_{ij}* with alkane carbon number for nitrogen/alkanes at various temperatures using the Peng–Robinson equation of state.

3. The basic conclusion of our work can be summarized as follows: In contrast to the *k_{ij}* parameter, the *n* exponent typically decreases with increasing asymmetry. Characteristic results are shown in Figure 7 for CO₂/alkanes, Figure 5 for nitrogen/alkanes, Figure 6 for

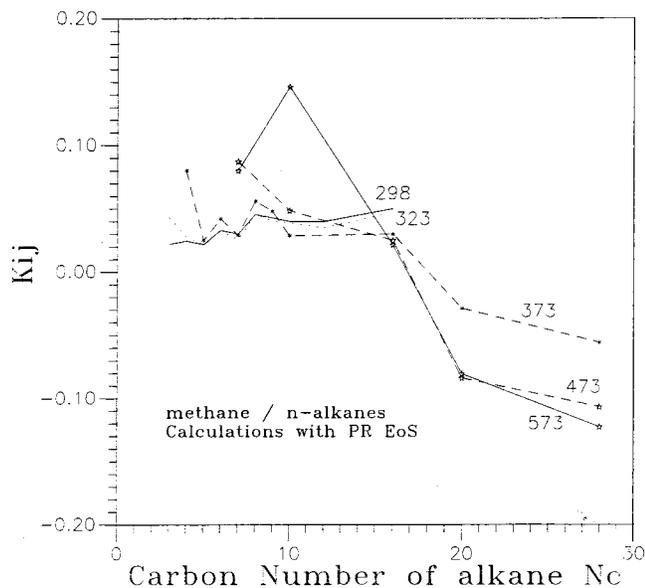


Figure 4. Plot of k_{ij} with alkane carbon number for methane/alkanes at various temperatures using the Peng-Robinson equation of state.

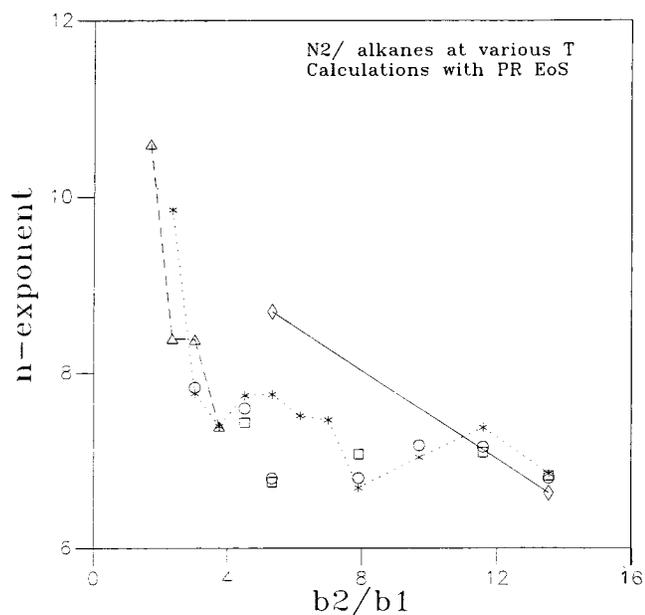


Figure 5. Plot of the n exponent with size asymmetry (ratio of critical co-volumes) for nitrogen/alkanes at various temperatures with the Peng-Robinson equation of state (triangles = 250 K, stars = 323 K, circles = 373 K, squares = 411, and rhombes = 497 K).

methane/alkanes, Figure 8 for H_2S /alkanes, and Figure 9 for many gas/alkane systems (using Henry's constants) including noble gases. Other gas/alkane systems, not shown here, for example, ethane and propane, behave similarly. This behavior of the n exponent is possibly due to the fact that use of the n exponent largely incorporates the size effects, not accounted when solely k_{ij} is employed.

4. As the asymmetry increases from gas/alkane to polymer solutions (Figure 11), the exponent n decreases and approaches the value of 3 for extremely asymmetric systems. Still, even for polymer solutions, the effect of polymer molecular weight is important and thus, for the less asymmetric systems, the n value is higher than 3, comparable to ordinary systems (Figure 11). For polymer blends (symmetric systems of two polymers of

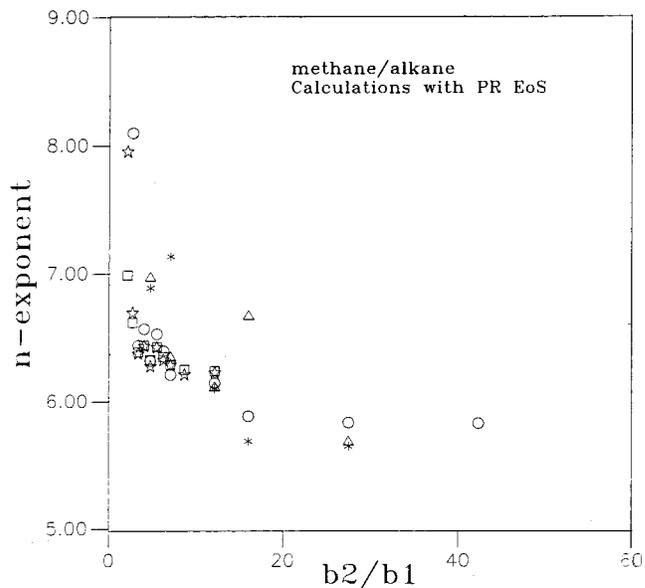


Figure 6. Plot of the n exponent with size asymmetry (ratio of critical co-volumes) for methane/alkanes at various temperatures with the Peng-Robinson equation of state (squares = 298 K, open stars = 323 K, circles = 373 K, triangles = 473 K, and closed stars = 573 K).

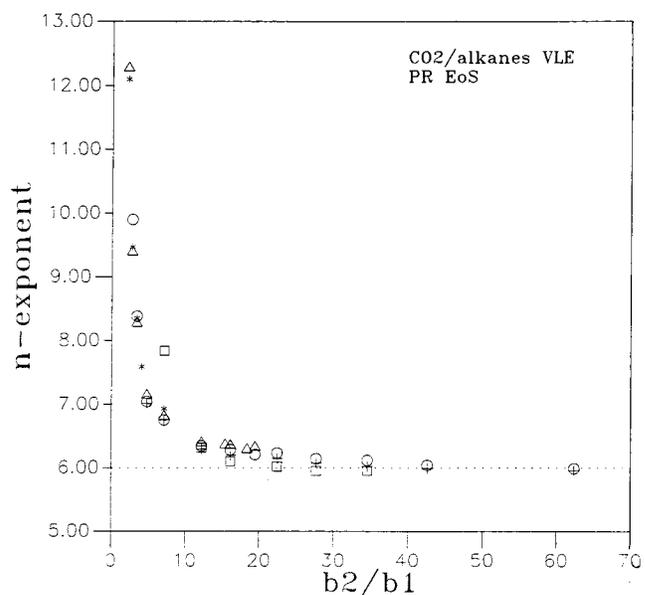


Figure 7. Plot of the n exponent with size asymmetry (ratio of critical co-volumes) for CO_2 /alkanes at various temperatures with the Peng-Robinson equation of state (stars = 298 K, triangles = 323 K, circles = 373 K, crosses = 423 K, and squares = 573 K).

usually similar molecular weights), the exponent n has, in the lines of this theory, values in the range of normal nonpolymeric systems (Figure 12).

5. Figures 10 and 13 present the n -exponent trend for two complex categories, alcohol/alkane solutions (calculations with the CPA equation) and CO_2 /solids (solid-gas equilibrium calculations with the PR equation). Again, the trend of the exponent is in agreement with its theoretical significance as discussed previously. For the solid systems, the n values are often higher than 6. This should be expected because for highly polar systems, as mentioned in the literature,²⁷ the exponent of the Mie potential has values near 7. It is interesting to note that, for many CO_2 /solid systems, the value of the exponent n is relatively constant, implying that a

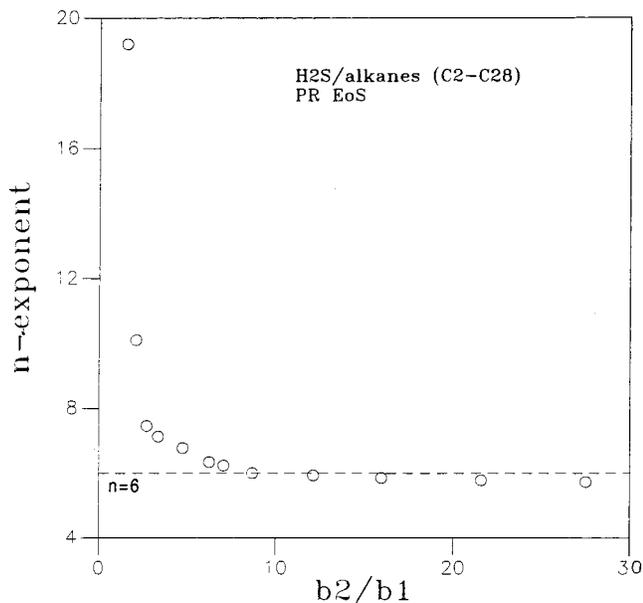


Figure 8. Plot of the n -exponent with size asymmetry (ratio of critical co-volumes) for H_2S /alkanes at various temperatures with the Peng-Robinson equation of state.

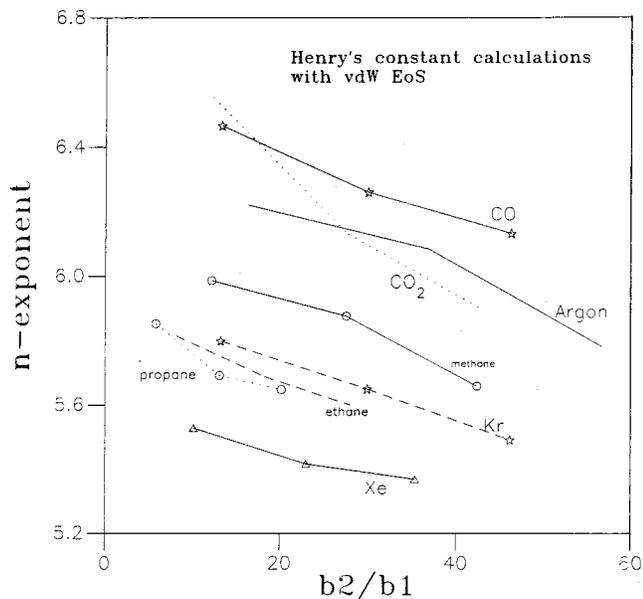


Figure 9. Plot of the n exponent with size asymmetry (ratio of critical co-volumes) for various gas/ n -alkanes using the van der Waals equation of state.

constant k_{ij} could be used for preliminary calculations.²⁰ For more precise calculations, two interaction parameters are often required.

6. A very important comment should be made for the rather symmetric systems (b_2/b_1 ratio between 1 and 2), where the n exponent that best fits the data receives rather high values, much above 6 (Figures 10 and 12). At a first glance, it would be difficult to explain this observation based on the London-Mie theory. For such symmetric systems, these high n values emphasize the problems of the GM rule to properly account for the energy differences of even simple molecules; such problems are possibly masked at higher asymmetries because of the rather good performance of the equation as size effects increase. Indeed, it seems reasonable to state the GM rule performs better in the medium-

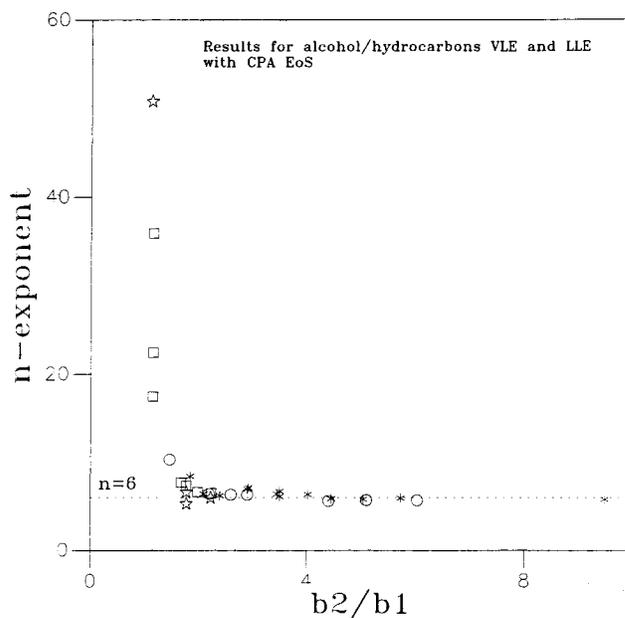


Figure 10. Plot of the n exponent with size asymmetry (ratio of critical co-volumes) for alcohol/alkane solutions with the CPA equation of state (closed stars = methanol/alkanes, circles = ethanol/alkanes, open stars = phenol/alkanes, and squares = various alcohols/hydrocarbons).

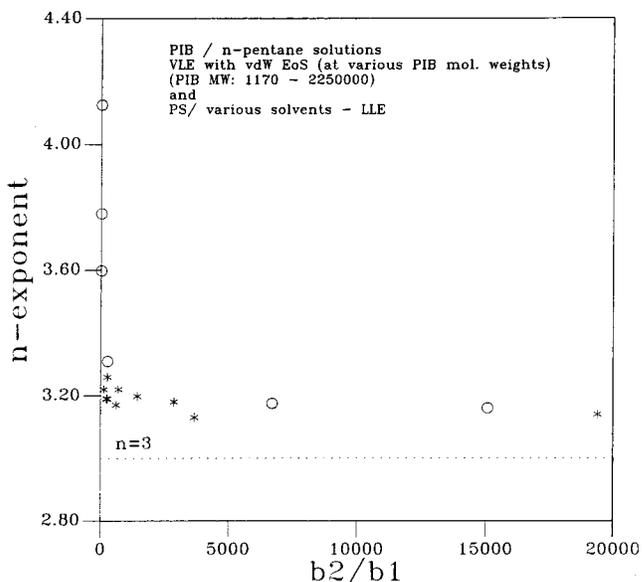


Figure 11. Plot of the n exponent with size-asymmetry (ratio of critical co-volumes) for polymer solutions with varying molecular weights with the van der Waals equation of state.

asymmetric region rather than for the very symmetric and for the very asymmetric systems.

7. Finally, a comment should be made for the rather peculiar mixing behavior of nitrogen/alkanes, that is, the systematic increase of the k_{ij} parameter with increasing chain length, even at high temperatures. This could be attributed to nitrogen's special features compared to other gases; it has the lowest critical temperature and consequently molecular energy parameter. Moreover, as mentioned by Lin and Parcher,¹³ the heat of solution in n -alkanes has a positive value compared to the negative values that characterize all other gas/alkane systems (e.g., Ar, Kr, Xe, CO_2 , methane, ethane, propane with n -alkanes).

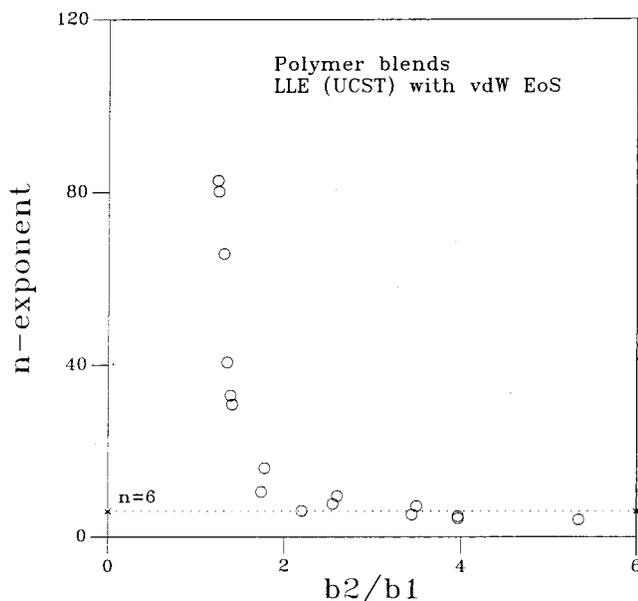


Figure 12. Plot of the n exponent with size asymmetry (ratio of critical co-volumes) for polymer blends with the van der Waals equation of state.

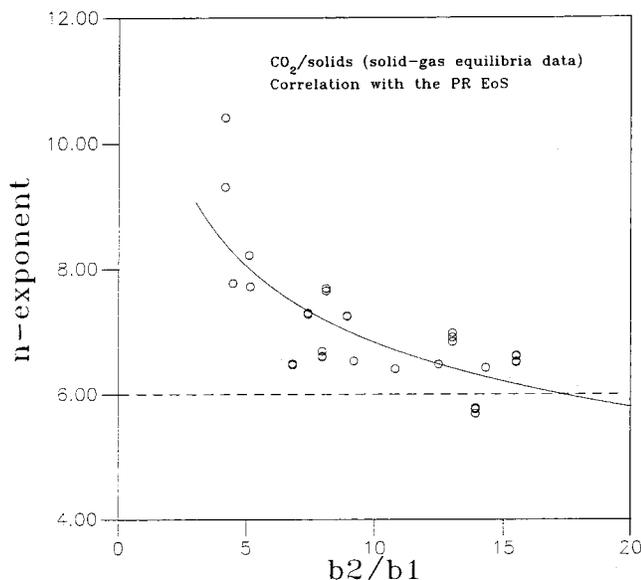


Figure 13. Plot of n exponent, obtained from solid-gas equilibrium data, with size asymmetry (ratio of critical co-volumes) for CO_2 /solids with the Peng-Robinson equation of state.

5. Conclusions

The basic findings of our work on the study of the GM rule for the cross-energy parameter for different types of systems can be summarized as follows:

i. The commonly employed k_{ij} interaction parameter is a strong function of both temperature and size difference between the components. The coupling of these effects make generalizations difficult. In fact, k_{ij} sometimes increases with size difference, for example, low temperatures and lower asymmetries, while in most other cases, it decreases with increasing asymmetry.

ii. In contrast to the behavior of k_{ij} , the n exponent of the general combining rule we presented here systematically decreases with size difference. It seems that the general combining rule incorporates the size effects and provides physically meaningful insight into equation of state behavior.

iii. The n exponent typically receives values (a) >6 , close to 7, for solid-gas systems (effect of polarity on the potential function), (b) 5–6 for medium asymmetric systems and polymer blends, (c) 4–3 for polymer solutions, and (d) ≥ 6 for very symmetric systems.

The above conclusions emphasize the importance of employing the n exponent as an adjustable parameter to derive generalized expressions for different gas/alkane systems and other types of systems. For the reasons explained above, it is expected that use of the n exponent may deprive these generalized expressions of the problems encountered with k_{ij} for the different gas/alkane categories, shown by several researchers.^{12,14,15}

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List of Abbreviations

AM = arithmetic-mean (combining rule)
 CPA = cubic-plus-association
 EoS = equation of state
 GM = geometric-mean (combining rule)
 PR = Peng-Robinson
 LLE = liquid-liquid equilibrium
 SAFT = statistical association fluid theory
 SGE = solid-gas equilibrium
 SRK = Soave-Redlich-Kwong
 UCST = upper critical solution temperature
 vdW = van der Waals
 VLE = vapor-liquid equilibrium

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