A Fully Consistent Approach for an Associate Solution Model

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Outline

Part 1

- Theoretical Limits for Configurational Entropy and Entropy Paradox
- Model Description
- Dilute Solutions
- Comparison with Similar Models

Part 2

- Geometric Models
- Power Series Models
- Probabilistic Interpretation

Part 1
Resolving Entropy Paradox

Theoretical Limits for Configurational Entropy

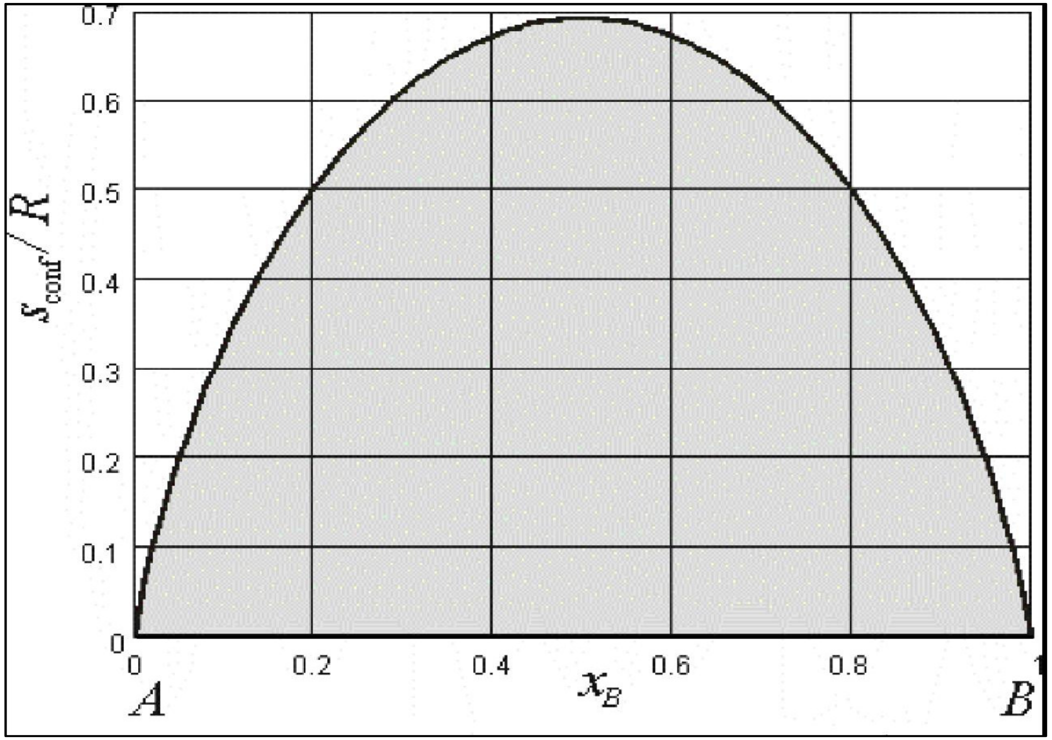
Entropy is a measure of disorder

Ideal solution - maximum disorder

For any solution phase: $S \leq S_{\text{ideal}}$

At the same time

$S \geq 0$

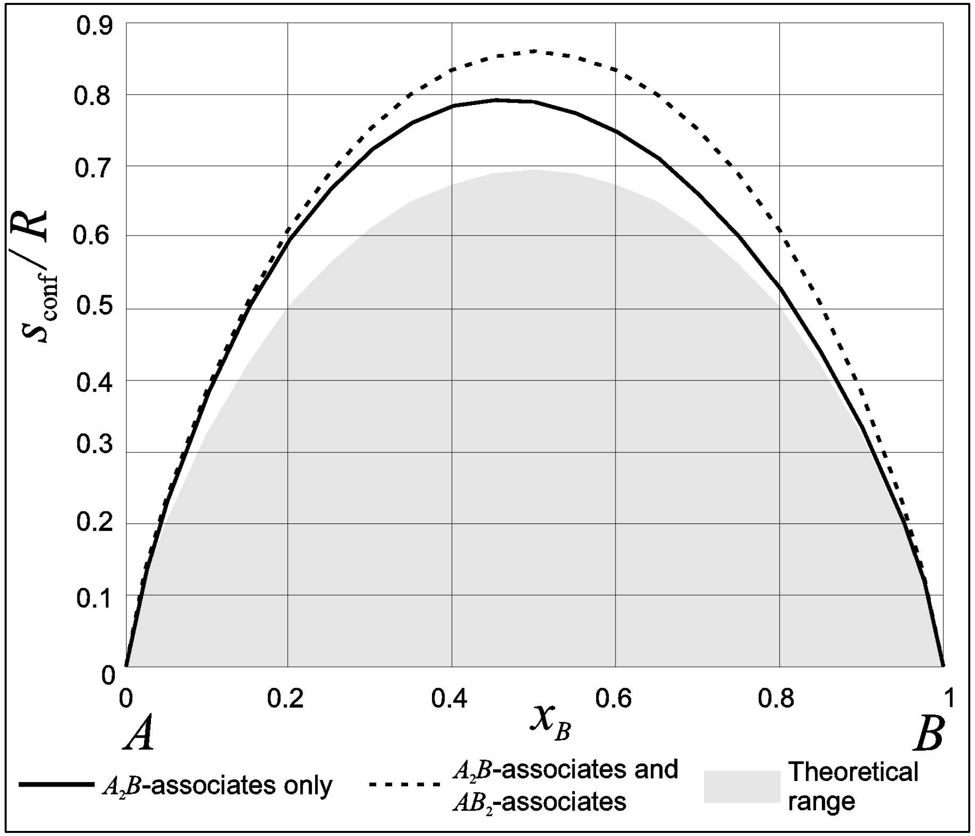


Entropy Paradox

Luck et al. 1989
High temperature limit

Pelton et al. 2000

$$\Delta g = 0$$



Model Assumptions

- Interactions between mixing particles result in the formation of associates which are at equilibrium with each other.
- Associates are uniformly distributed (ideally mixed) over a lattice.
- All pure solution components and the chemical solution of these components are treated in a **unified way** (associates of the same size).
- Particles of the same type are indistinguishable, while particles of different types and particle sites within an associate are distinguishable.

Model Description

The system A-B with 3-particle associates

1	2	3
[A	A	A]
[A	A	B]
[A	B	A]
[B	A	A]
[A	B	B]
[B	A	B]
[B	B	A]
[B	B	B]

$$\Omega = \frac{\left(N_0 \sum_{i,j,k=\mathrm{A,B}} n_{[ijk]}\right)!}{\prod_{i,j,k=\mathrm{A,B}} \left(N_0 n_{[ijk]}\right)!}$$

$$G = \sum_{i,j,k=\mathrm{A,B}} n_{[ijk]} \left(g_{[ijk]} + RT \ln(x_{[ijk]})\right)$$

$$\left(\frac{\partial G}{\partial n_{[ijk]}}\right)_{n_\mathrm{A}, n_\mathrm{B}, n_{[i'j'k']}} = 0$$

$$S_\mathrm{conf} = k_\mathrm{B} \ln(\Omega)$$

$$\frac{2}{3}[\mathrm{AAA}] + \frac{1}{3}[\mathrm{BBB}] \leftrightarrow [\mathrm{AAB}]$$

$$\Delta g_{[\mathrm{AAB}]} = g_{[\mathrm{AAB}]} - \frac{2}{3} g_{[\mathrm{AAA}]} - \frac{1}{3} g_{[\mathrm{BBB}]}$$

Model Description

The system A-B with 3-particle associates

$$g_{[AAB]} = g_{[ABA]} = g_{[BAA]} = g_{A_2B}; \quad g_{[BBA]} = g_{[BAB]} = g_{[ABB]} = g_{B_2A}$$

[A A A] - A_3 (pure A)

[A A B], [A B A], [B A A] } A_2B

[A B B], [B A B], [B B A] } AB_2

[B B B] - B_3 (pure B)

$$G = n_{A_3} g_{A_3} + n_{B_3} g_{B_3} + n_{A_2B} g_{A_2B} + n_{AB_2} g_{AB_2} + RT\left(n_{A_3}\ln(x_{A_3}) + n_{B_3}\ln(x_{B_3})\right) + RT\left(n_{A_2B}\ln\left(\frac{x_{A_2B}}{3}\right) + n_{AB_2}\ln\left(\frac{x_{AB_2}}{3}\right)\right)$$

$$\left(\frac{\partial G}{\partial n_{A_2B}}\right)_{n_A, n_B, n_{AB_2}} = \left(\frac{\partial G}{\partial n_{AB_2}}\right)_{n_A, n_B, n_{A_2B}} = 0$$

Model Description

The system A-B with 3-particle associates

$$\Delta g_{A_2B} = \Delta g_{B_2A} = 0$$

$$x_{A_3} = x_A^3$$

$$x_{A_2B} = 3x_A^2 x_B$$

$$x_{AB_2} = 3x_A x_B^2$$

$$x_{B_3} = x_B^3$$

G **expression correctly reduces to the ideal solution**

Dilute Solutions

Solution of monoparticles A and B and associates A_2B

with $\Delta g_{A_2B} \rightarrow -\infty$

For small x_A $a_B \approx 1 - \frac{x_A}{2}$

Rault's law $a_B \approx 1 - x_A$

$\Delta g_{A_2B} = -\infty$

For any finite Δg_{A_2B}

Rigorously proven for CAM and MAF

Models Comparison

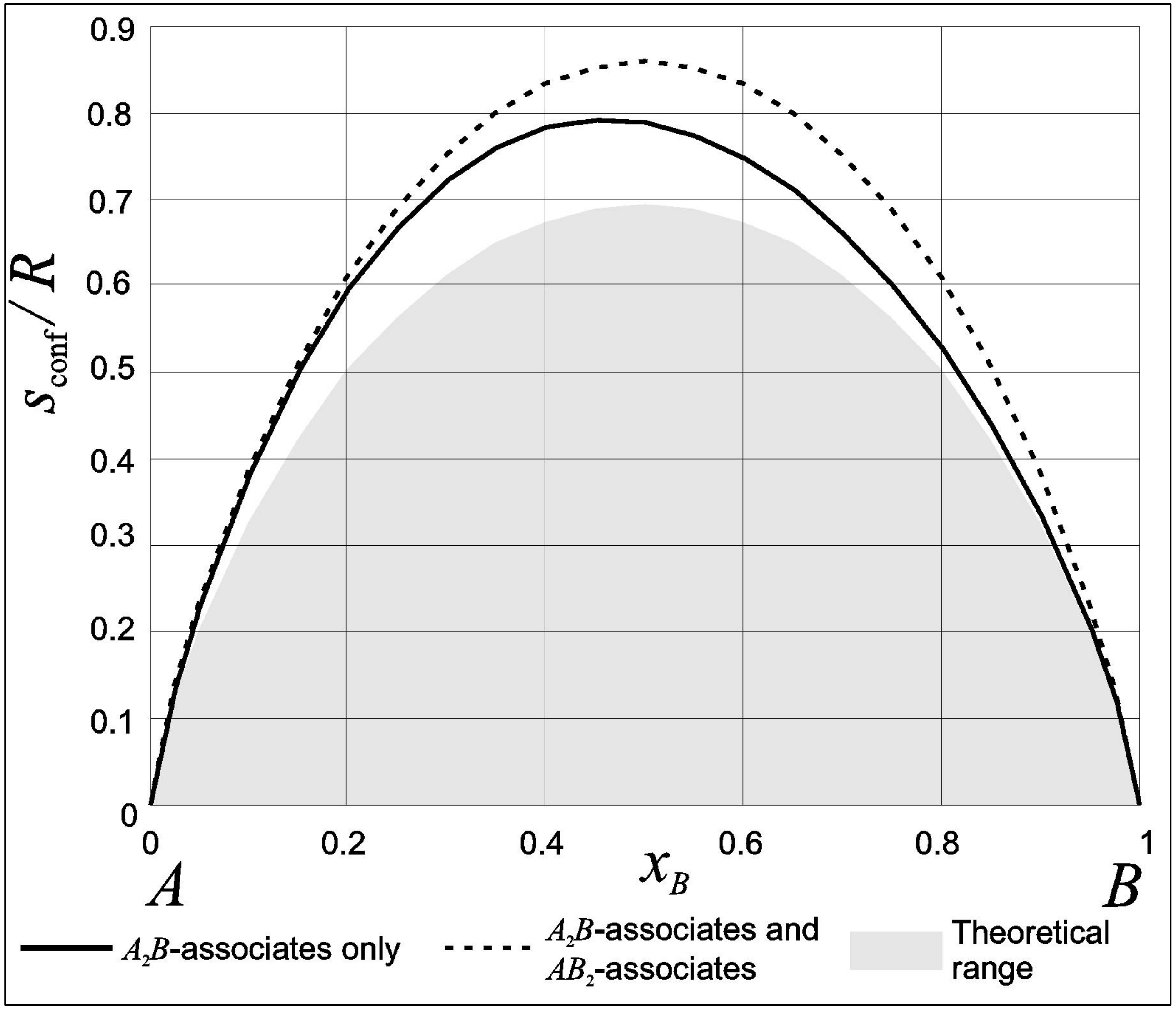
Models

- CAM
- ASM
- MQM 1986
- MQM 2000
- MAF

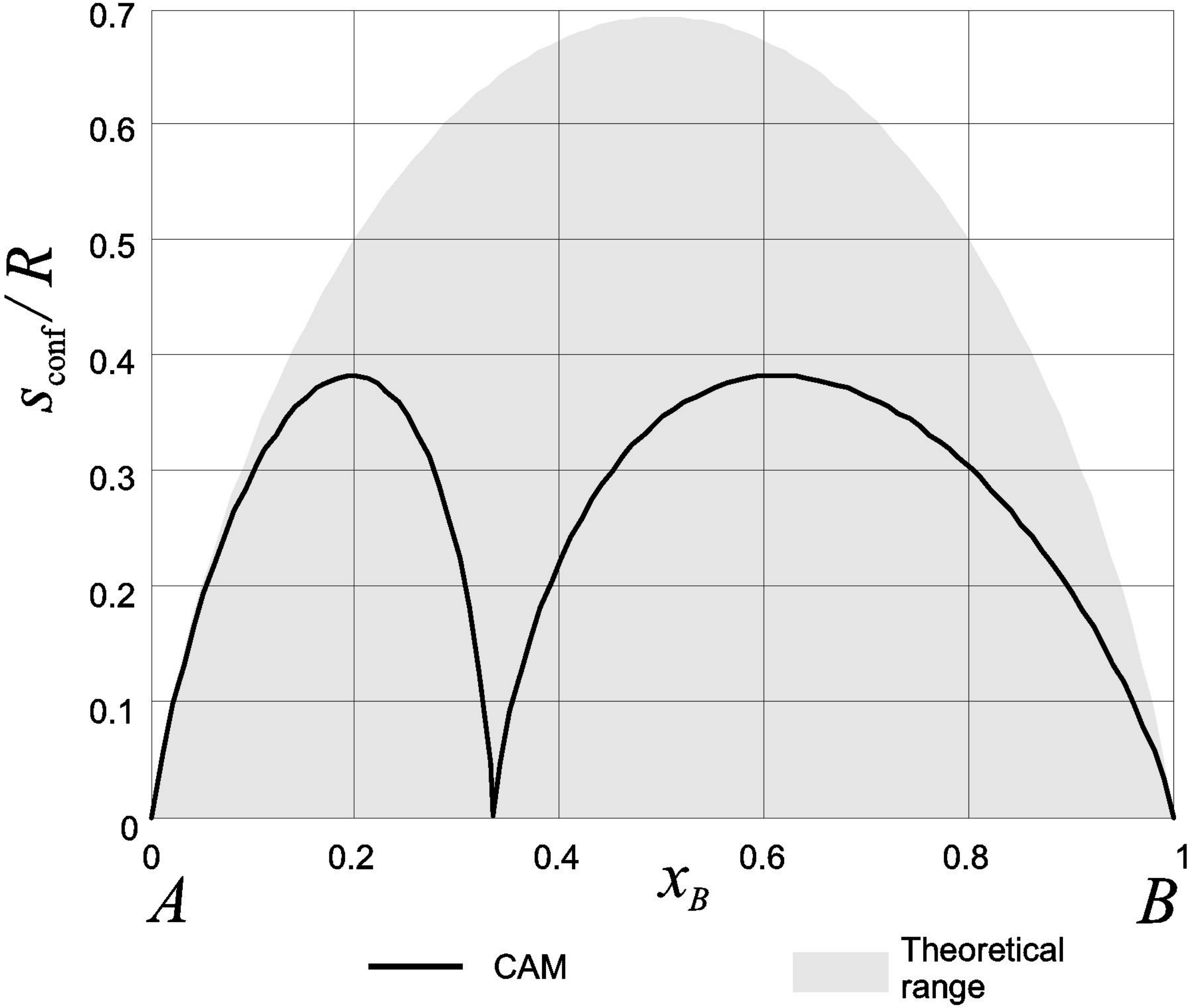
Conf. Entropy

- Ideal solution
- Highly ordered solution
- Immiscible components

CAM (Ideal)

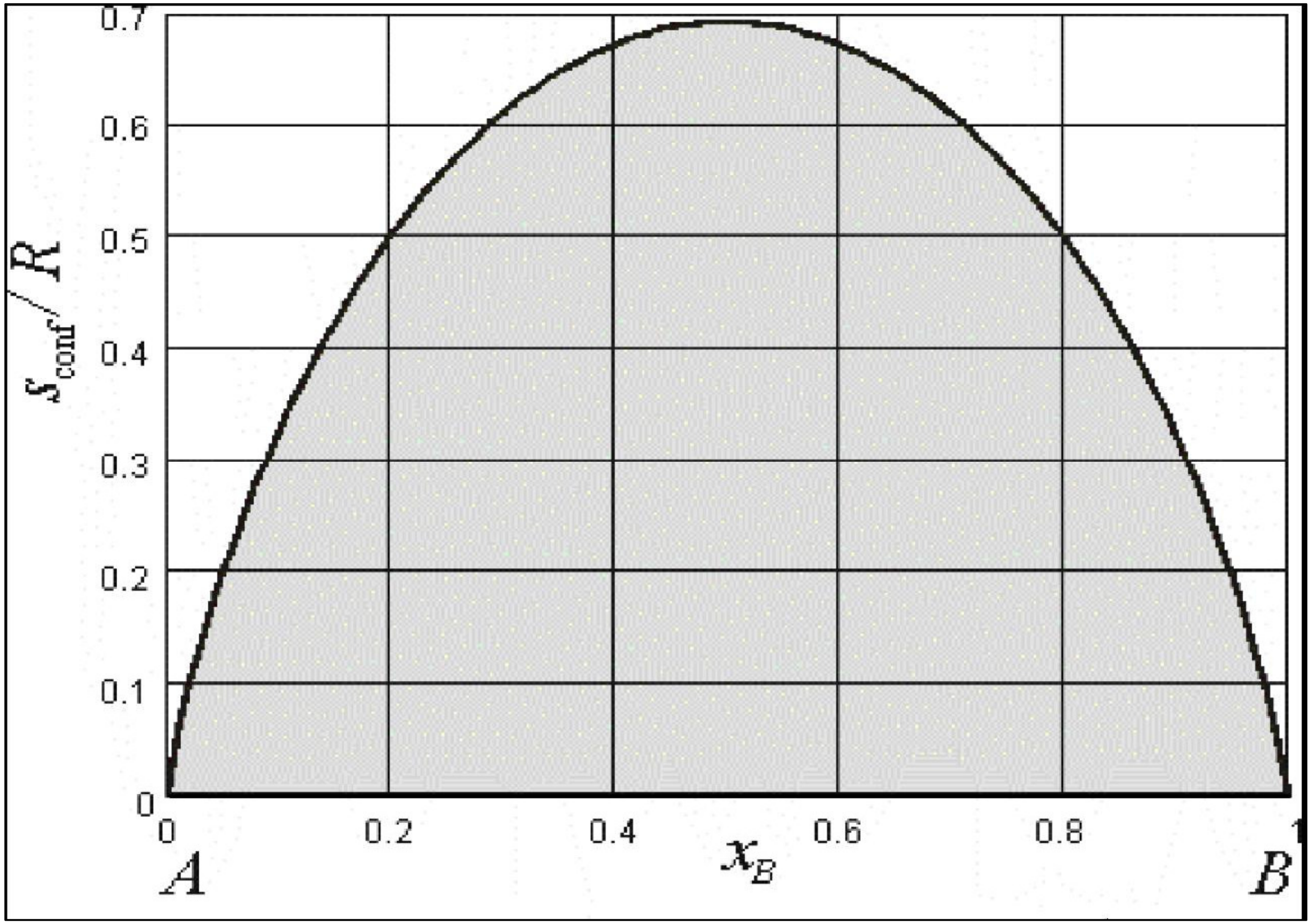

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
s_{conf}/R
0
0.2
0.4
0.6
0.8
1
x_B
A
B
A_2B-associates only
A_2B-associates and AB_2-associates
Theoretical range

CAM (Ordered)

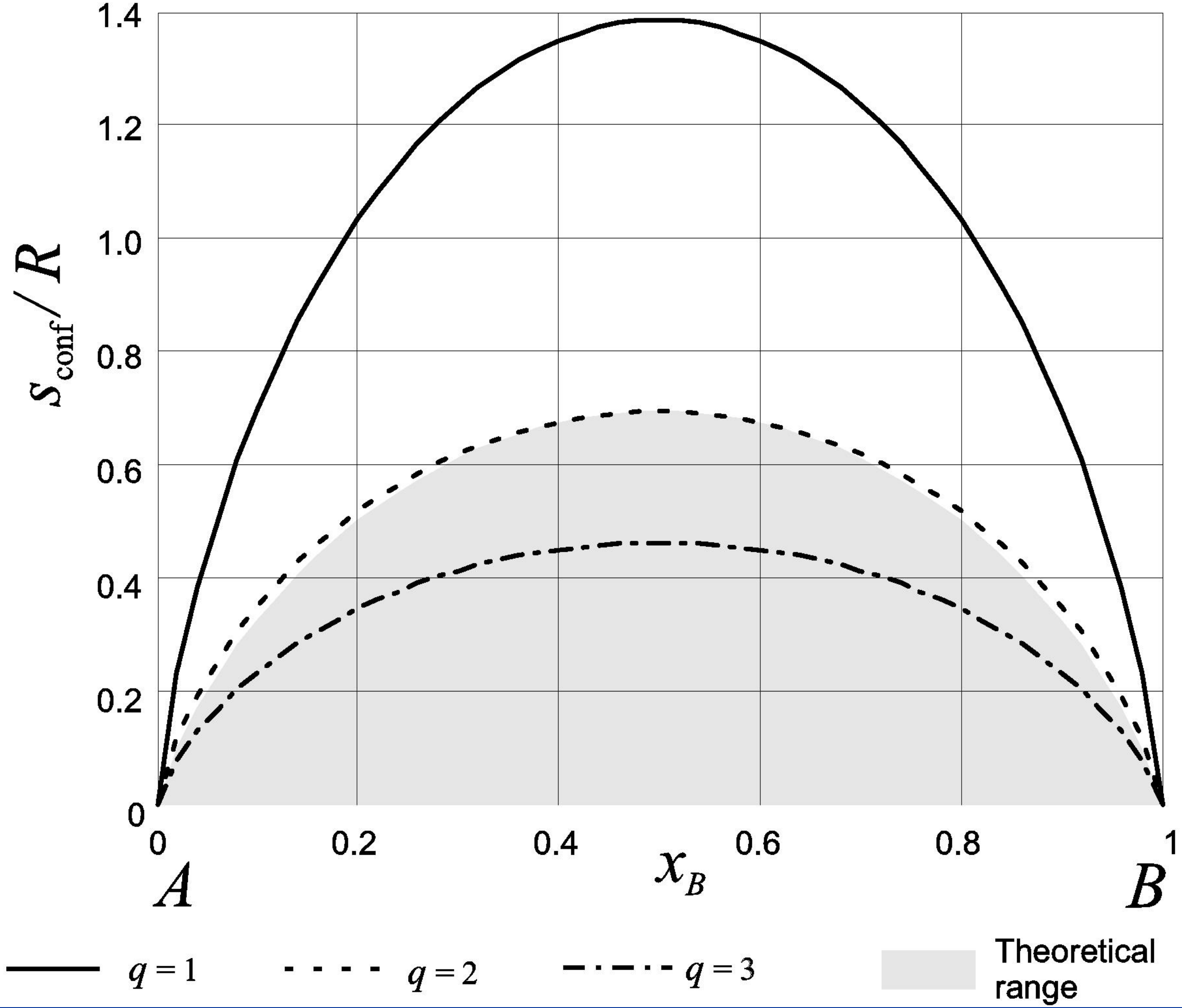


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
s_{conf}/R
0
0.2
0.4
0.6
0.8
1
x_B
A
B
CAM
Theoretical range

CAM (Immiscible)

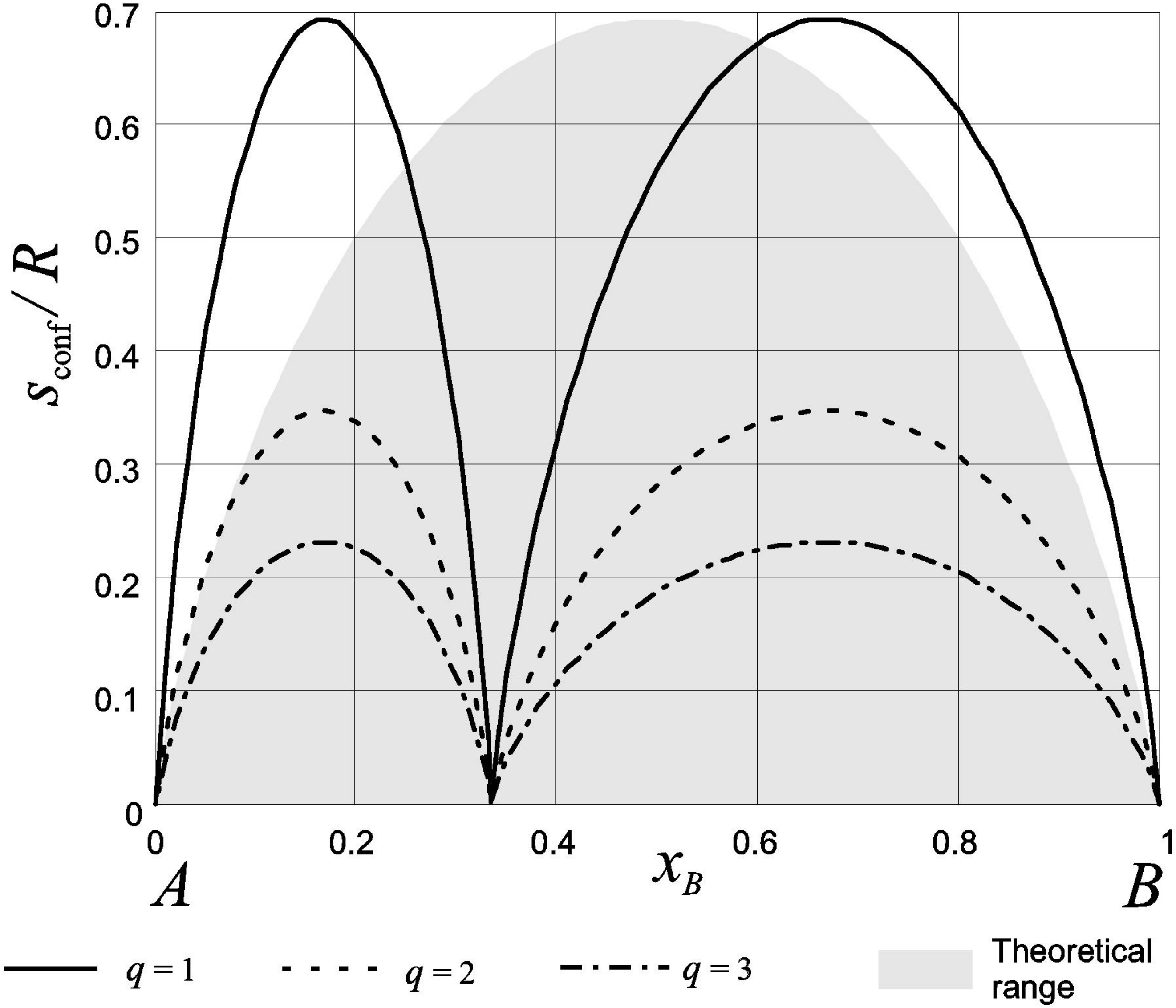


ASM (Ideal)



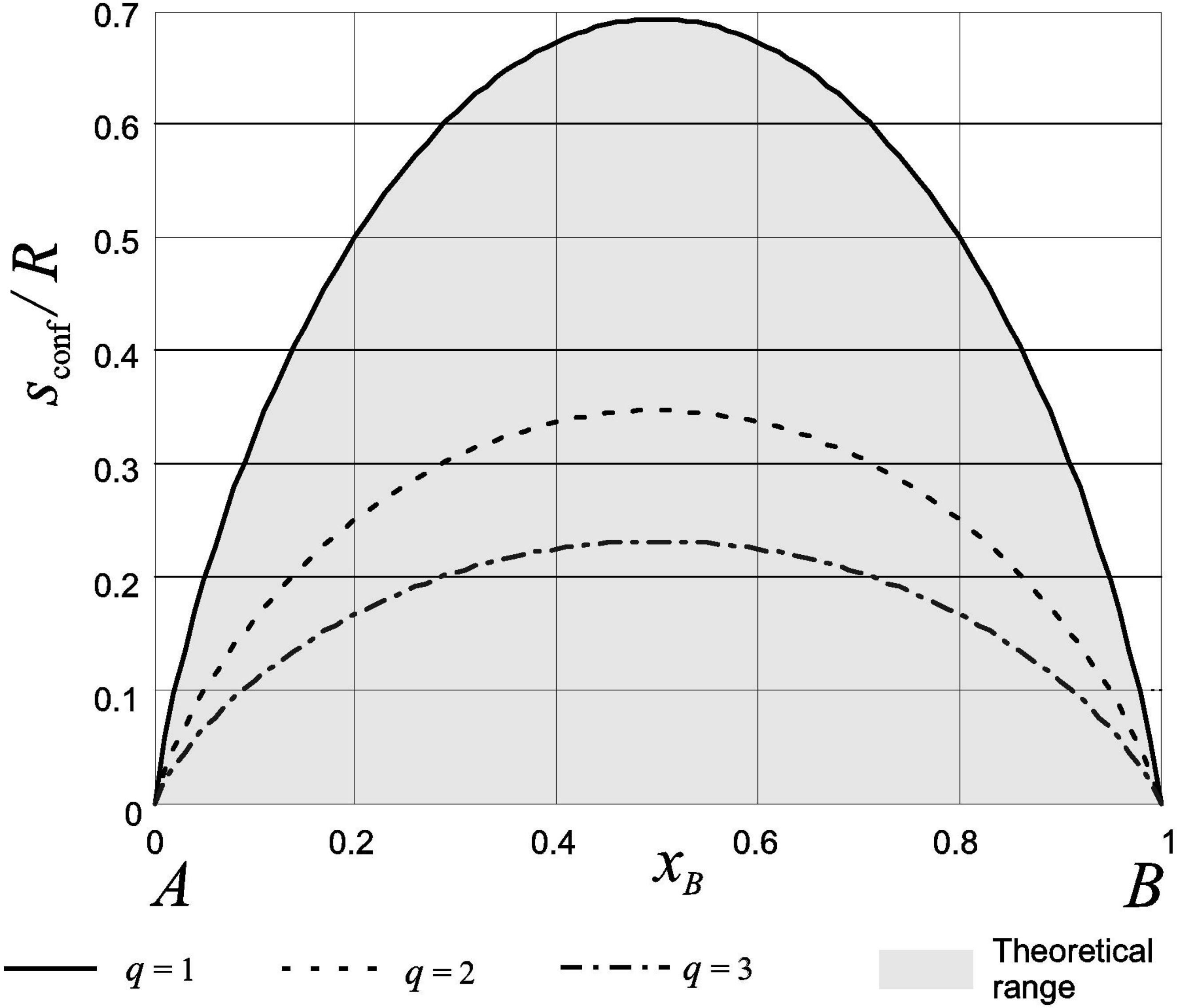
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
s_{conf}/R
0
0.2
0.4
0.6
0.8
1
x_B
A
B
$q = 1$
$q = 2$
$q = 3$
Theoretical range

ASM (Ordered)

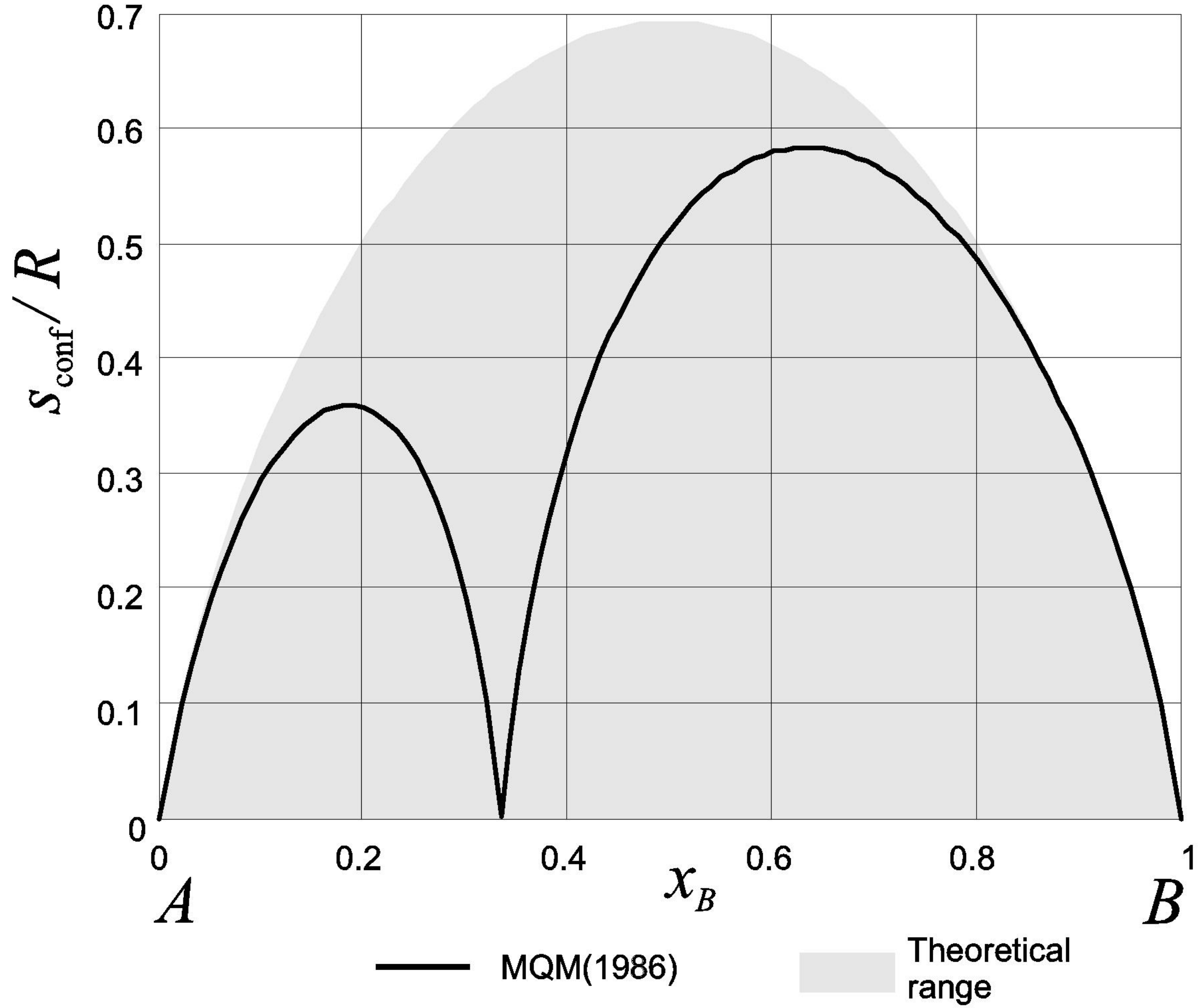


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
s_{conf}/R
0
0.2
0.4
0.6
0.8
1
x_B
A
B
$q = 1$
$q = 2$
$q = 3$
Theoretical range

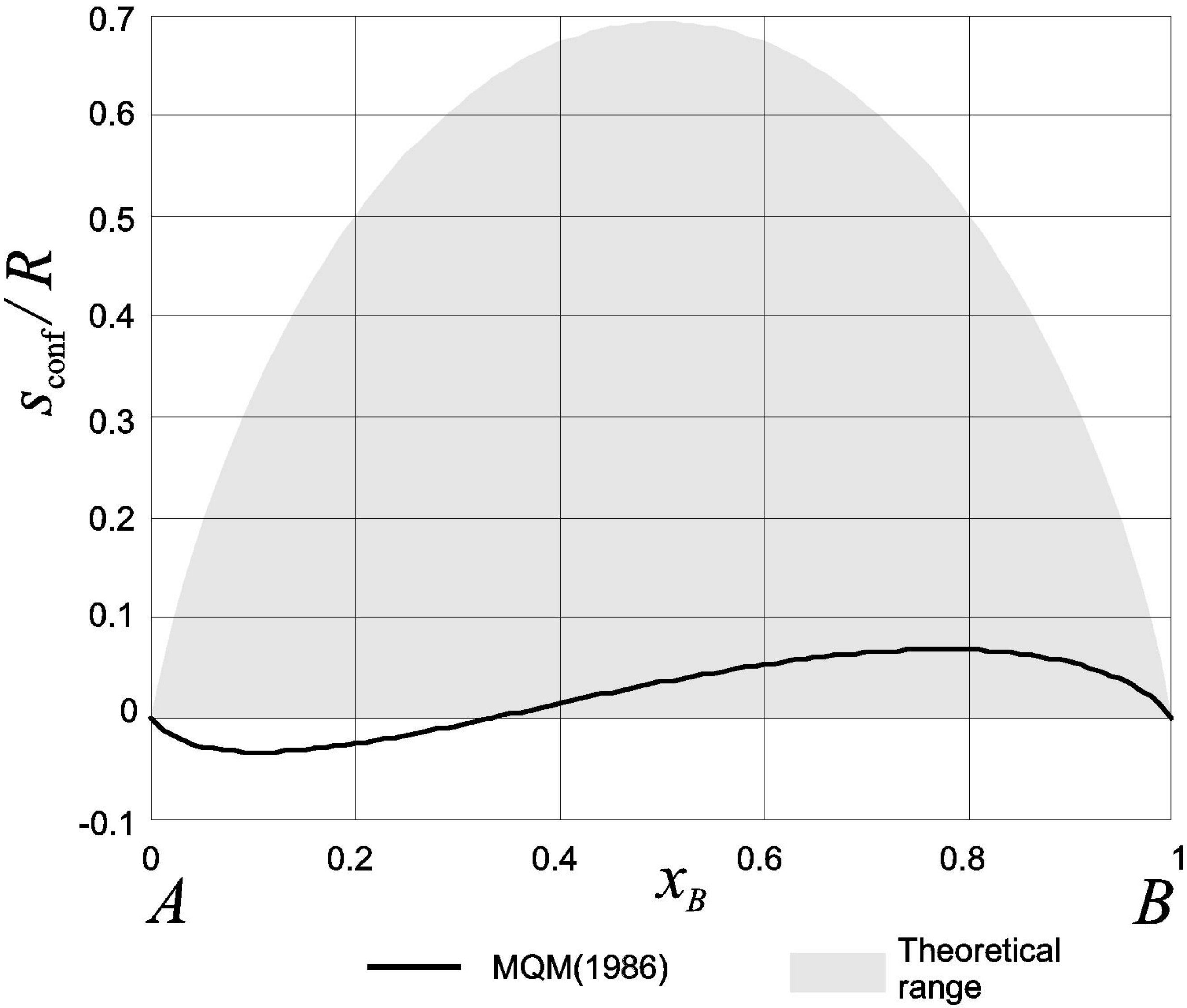
ASM (Immiscible)



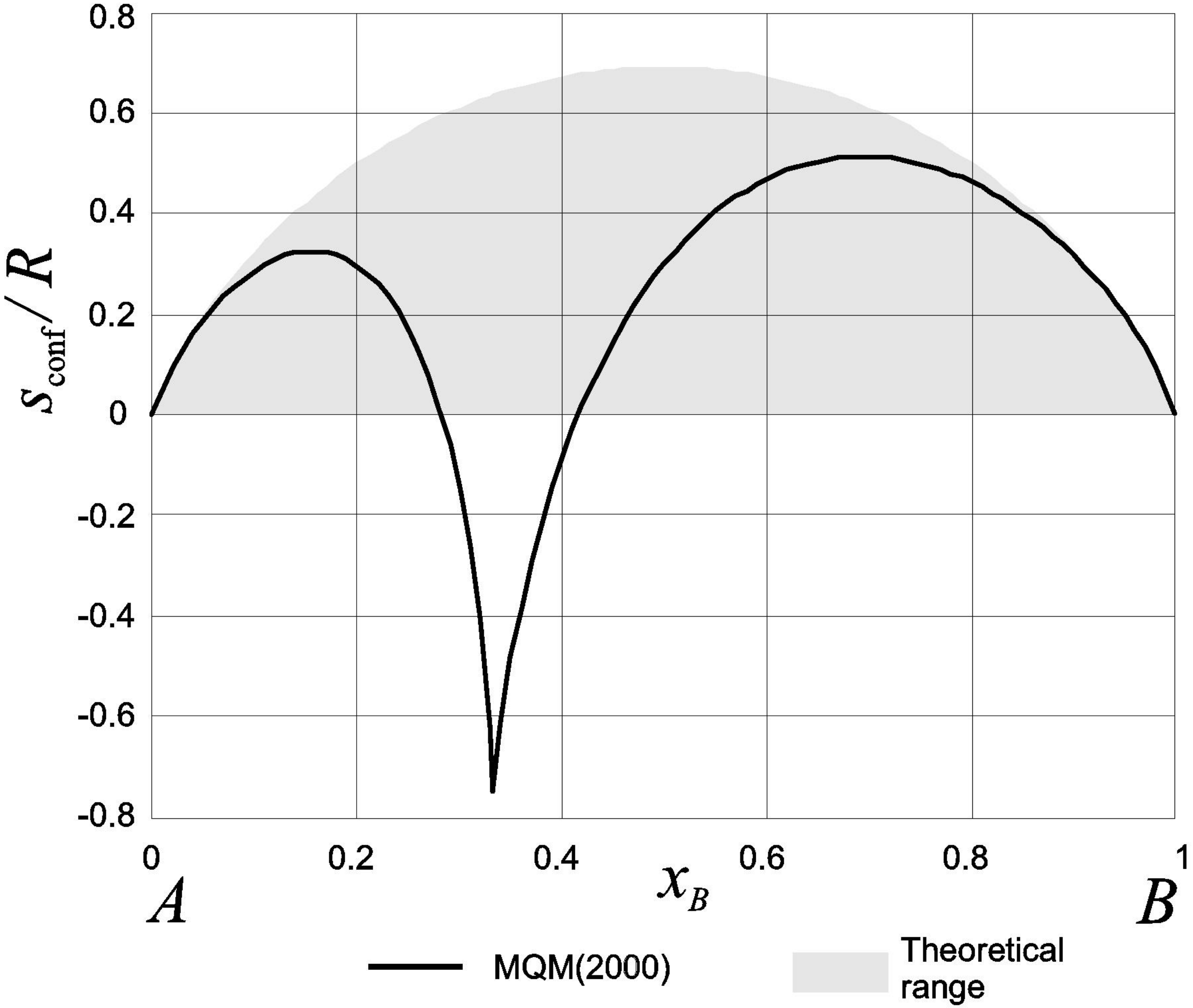
MQM 1986 (Ordered)



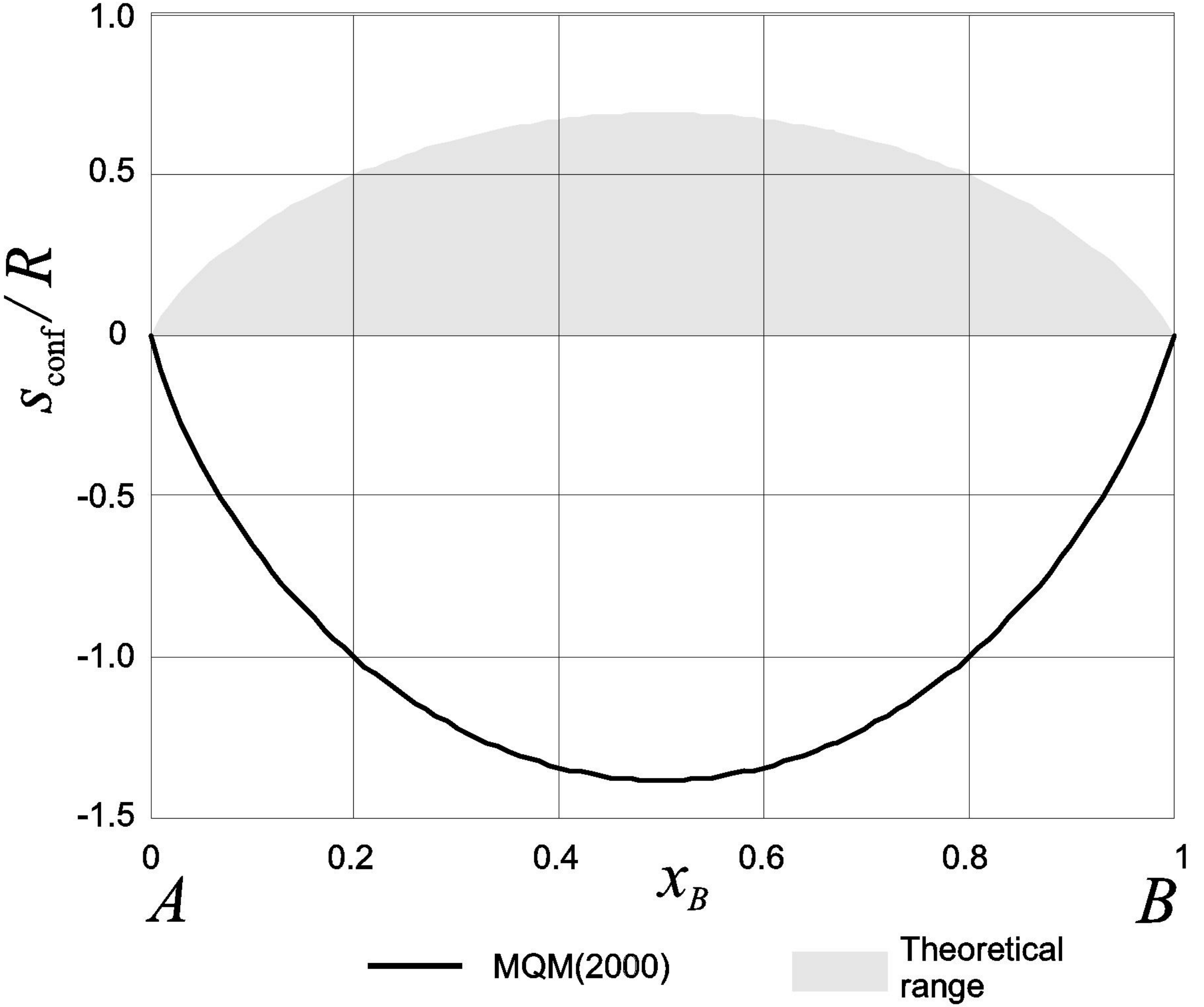
MQM 1986 (Immiscible)



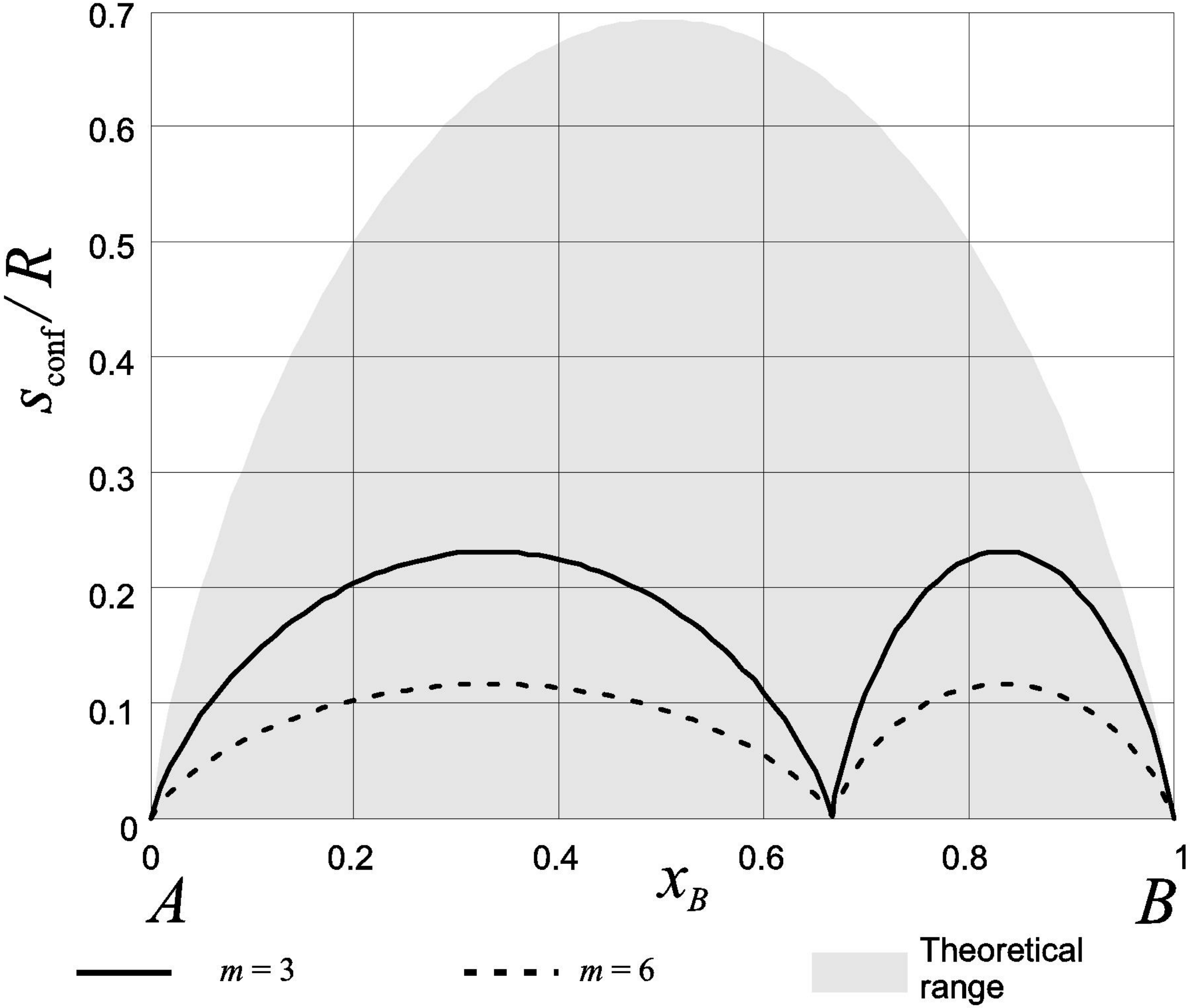
MQM 2000 (Ordered)



MQM 2000 (Immiscible)



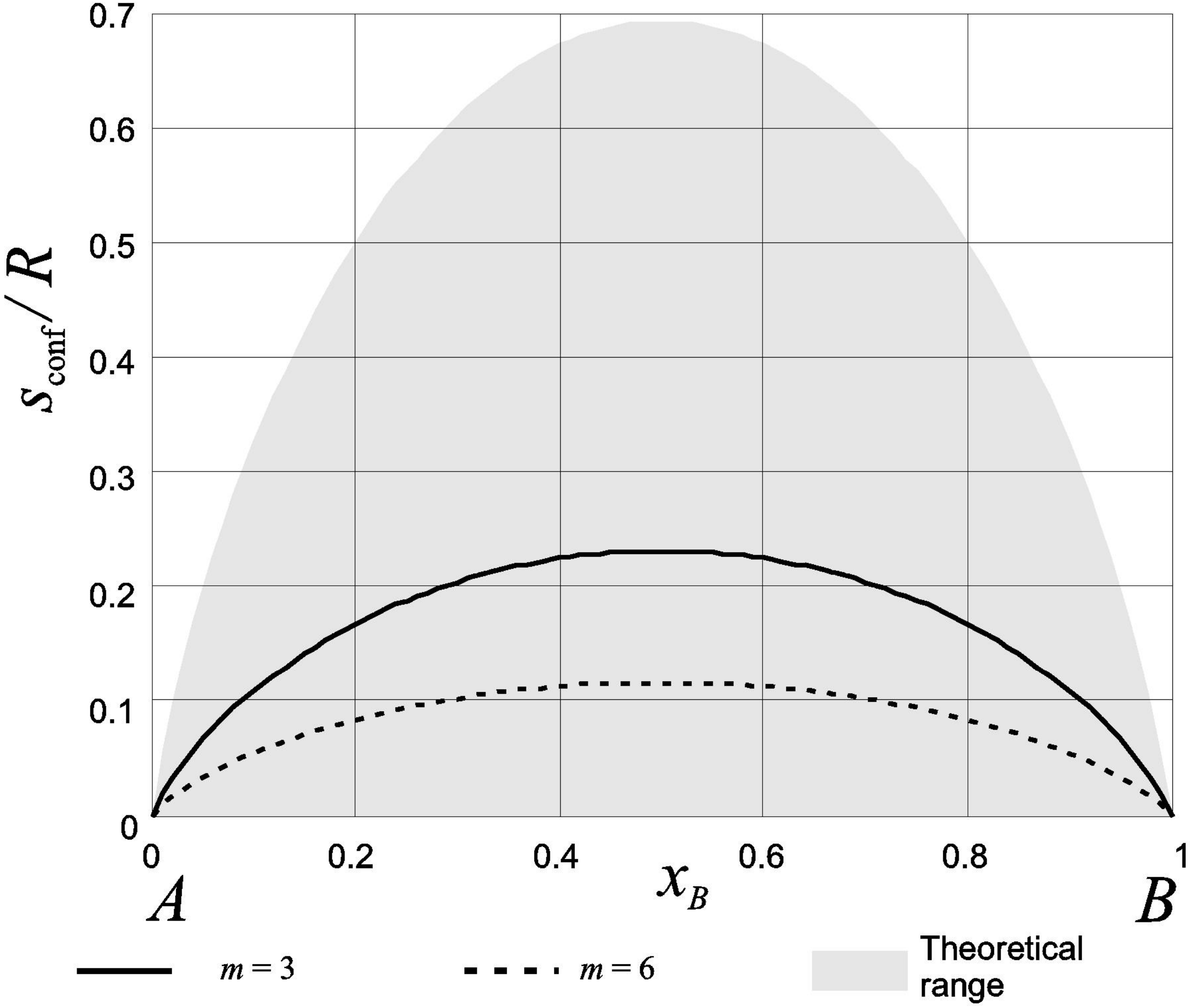
MAF (Ordered)



0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
s_{conf}/R
0
0.2
0.4
0.6
0.8
1
x_B
A
B
$m = 3$
$m = 6$
Theoretical range

MAF (Immiscible)

GTT-Technologies



Classical QM

Theoretically sound

- Ideal Solution ✓
- Ordered solution ✓
- Immiscible components (S=0) ✓

However

Limited applicability

Other Properties

	CAM	ASM	MAF	MQM1	MQM2
Free from entropy paradox	-	-	+	-	-
Raoult's law	+	-+	+	+!	+!
Selection CMO (binary systems)	+	+	+	+-	+
Selection CMO (multicomponent systems)	+	+	+	-	-
Clear physical meaning of the adjustable parameters	+	+	+	-	-

Correct G-expression MQM 2000

$$\frac{1}{Z_{\mathrm{A}}} = \frac{1}{Z_{\mathrm{AA}}^{\mathrm{A}}} \frac{2n_{\mathrm{AA}}}{2n_{\mathrm{AA}} + n_{\mathrm{AB}}} + \frac{1}{Z_{\mathrm{AB}}^{\mathrm{A}}} \frac{n_{\mathrm{AB}}}{2n_{\mathrm{AA}} + n_{\mathrm{AB}}}$$

$$\frac{1}{Z_{\mathrm{B}}} = \frac{1}{Z_{\mathrm{BB}}^{\mathrm{B}}} \frac{2n_{\mathrm{BB}}}{2n_{\mathrm{BB}} + n_{\mathrm{AB}}} + \frac{1}{Z_{\mathrm{BA}}^{\mathrm{B}}} \frac{n_{\mathrm{AB}}}{2n_{\mathrm{AA}} + n_{\mathrm{AB}}}$$

$$G = n_{\mathrm{A}} g_{\mathrm{A}}^{\circ} + n_{\mathrm{B}} g_{\mathrm{B}}^{\circ} - T\Delta S^{\mathrm{conf}} + \frac{n_{\mathrm{AB}}}{2} \Delta g_{\mathrm{AB}}$$

In error

Correct expression

$$G = \frac{Z_{\mathrm{A}}}{Z_{\mathrm{AA}}^{\mathrm{A}}} n_{\mathrm{A}} g_{\mathrm{A}}^{\circ} + \frac{Z_{\mathrm{B}}}{Z_{\mathrm{BB}}^{\mathrm{B}}} n_{\mathrm{B}} g_{\mathrm{B}}^{\circ} - T\Delta S^{\mathrm{conf}} + \frac{n_{\mathrm{AB}}}{2} \Delta g_{\mathrm{AB}}$$

Part 2
Treatment of polynomial excess functions

Model Used

Cheng and Ganguly:
"a major problem in solution thermodynamics"

Power Series

- **Margules**
- **Wohl**
- **Helffrich and Wood**
- **others**

Empirical

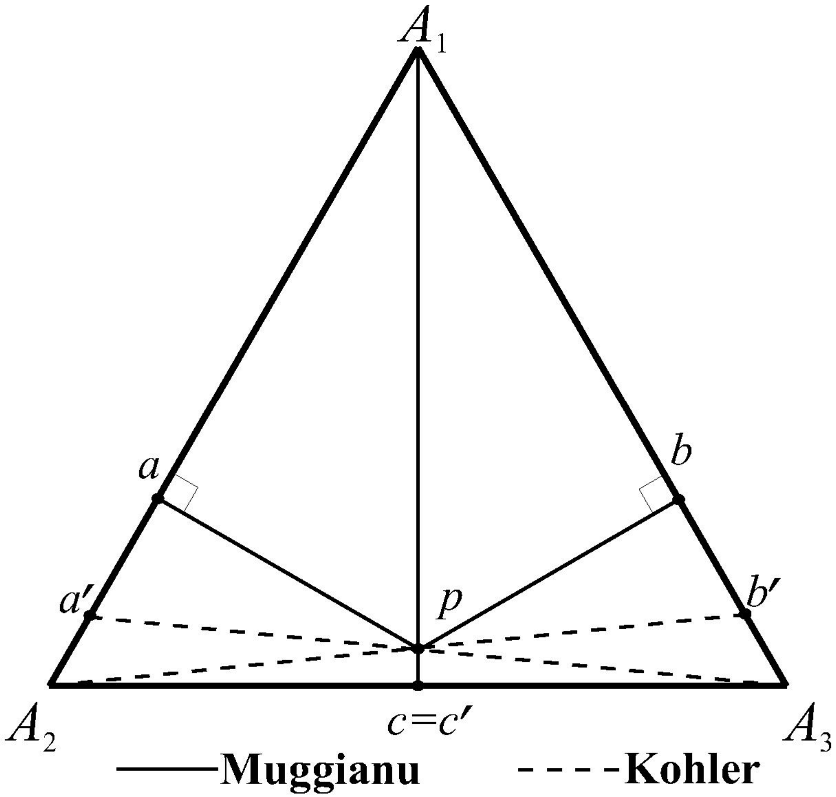
Geometric $\alpha_{12} x_1 x_2$

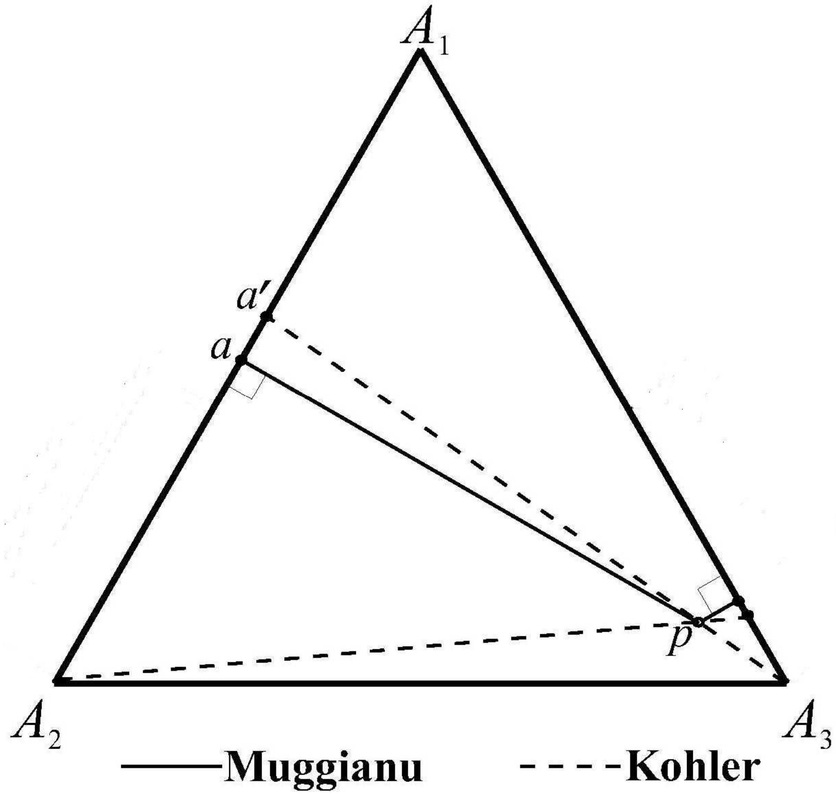
- **Kohler**
- **Muggianu (Hillert)**
- **Kohler / Toop**
- **Muggianu / Toop**

Inline with Calphad approach

Kohler vs Muggianu

Dilute solution (Chartrand and Pelton)

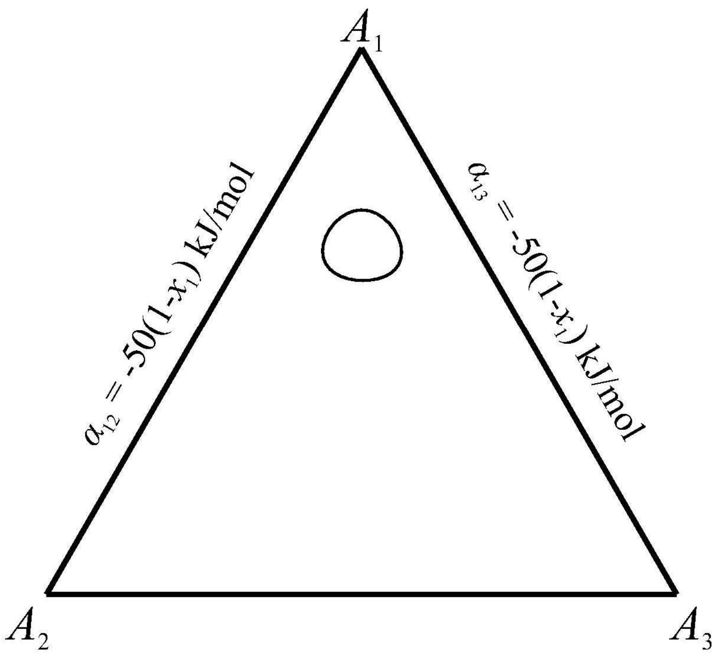




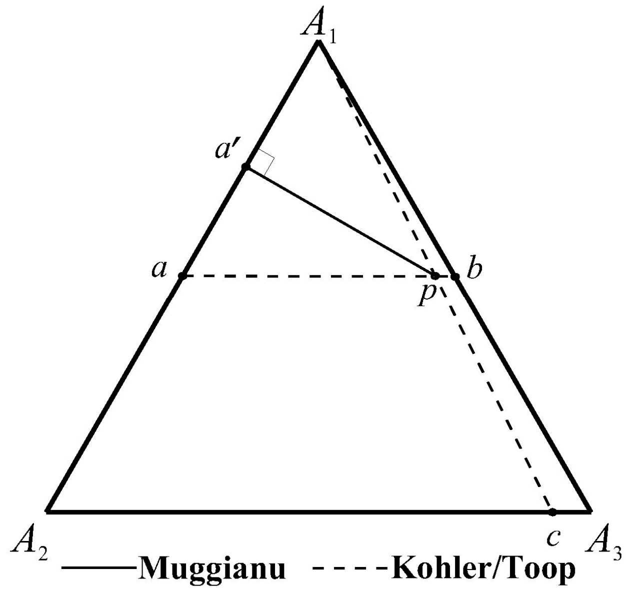
Kohler: singularities at terminal composition (Brynestad)

should not be used (Howald and Row)

Symmetric vs Asymmetric



Dilute solution



- **No quantitative criteria**
- **Chemically dissimilar components are treated in a thermodynamically different way**
- **Muggianu with the specially selected ternary term resolves the issue**

Power Series vs Geometric

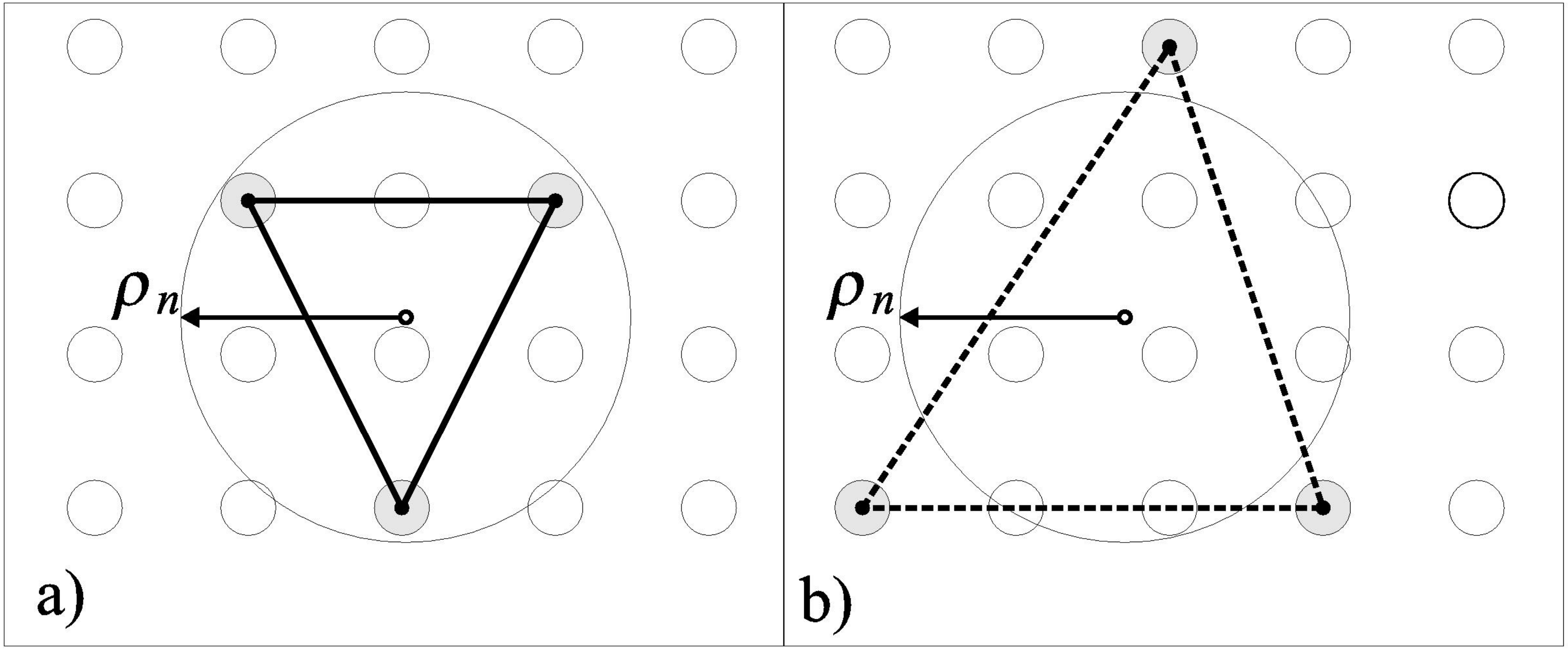
Helffrich and Wood:

- Subregular model - 3-particle interactions
- Ternary terms exist independently of the properties
- of the bounding binaries
- Ternary terms could be required even for Regular model

Power Series	Geometric
integral part	empirical

Probabilistic Interpretation

- **The Bragg-Williams approximation**
- **Short-range interaction** ρ_n
- **Uniform lattice** z_n



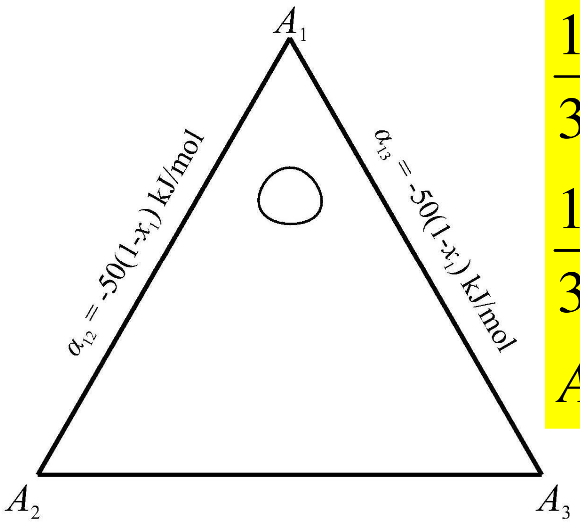
Probabilistic Interpretation

$$g = \sum_{i=1}^{r} x_i \left(g_i + RT \ln(x_i) \right) + \sum_{k_1 + \ldots + k_r = n} c_{n;k_1,\ldots,k_r} x_1^{k_1}, \ldots, x_r^{k_r}$$

$$c_{n;k_1,\ldots,k_r} = \frac{n!}{k_1!, \ldots, k_r!} \frac{z_n N_0}{n} \Delta g_{n;k_1,\ldots,k_r}$$

$$\frac{k_1}{n} A_1 \ldots A_1 + \ldots + \frac{k_r}{n} A_r \ldots A_r \leftrightarrow A_1 \ldots A_1 \ldots A_r \ldots A_r$$

Probabilistic Interpretation



$$\frac{1}{3}A_1A_1A_1 + \frac{2}{3}A_2A_2A_2 \leftrightarrow A_1A_2A_2; \qquad \Delta g = -\frac{50}{z_3N_0}\,\text{kJ/mol}$$

$$\frac{1}{3}A_1A_1A_1 + \frac{2}{3}A_3A_3A_3 \leftrightarrow A_1A_3A_3; \qquad \Delta g = -\frac{50}{z_3N_0}\,\text{kJ/mol}$$

$$A_2A_2 + A_3A_3 \leftrightarrow 2A_2A_3; \qquad \Delta g = 0$$

$$A_1(A_2A_2) + A_1(A_3A_3) \leftrightarrow 2A_1(A_2A_3); \quad \Delta g = 0$$

$$\frac{1}{3}A_1A_1A_1 + \frac{1}{3}A_2A_2A_2 + \frac{1}{3}A_3A_3A_3 \leftrightarrow A_1A_2A_3; \qquad \Delta g = -\frac{50}{z_3N_0}\,\text{kJ/mol}$$

$${}^{\text{Ex}}g = -50x_1(1-x_1)^2\,\text{kJ}$$