Predicting Fick- and Maxwell-Stefan diffusivities in liquids

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Ind. Eng. Chem. Res., 2011, 50, 10350-10358.

Collaborators

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- Sondre K. Schnell (Delft)
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(Empirical) Fick formulation for multicomponent diffusion

$$J_i = -c_t \sum_{k=1}^{n-1} D_{ik} \nabla x_k$$

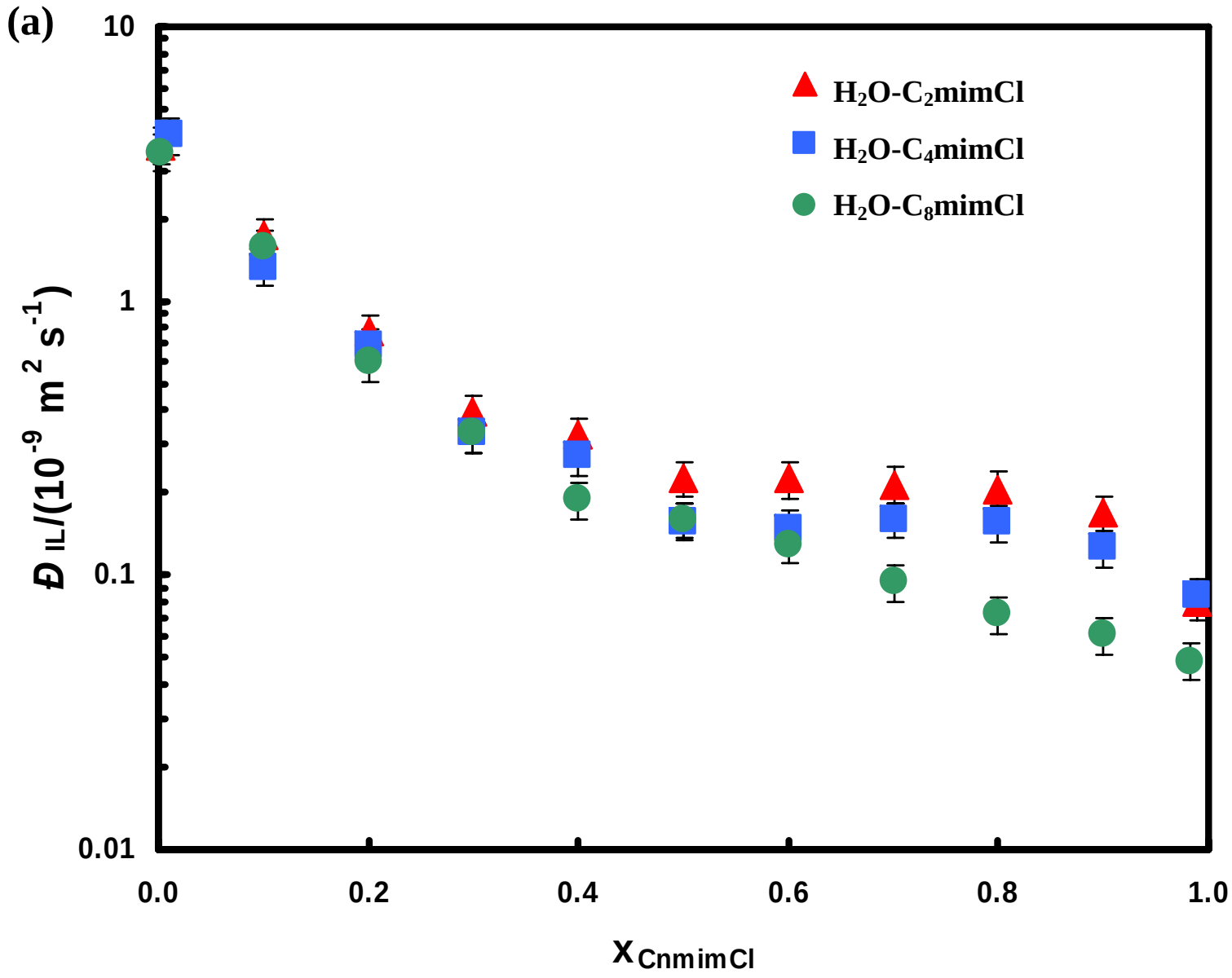
- n components, $(n-1)^2$ Fick diffusivities
- $\sum_{i=1}^{n} J_i = 0$ (molar reference frame)
- $D_{ij} \neq D_{ji}$ for $n > 2$
- D_{ij} strongly dependent on the mole fractions $x_1 \cdots x_n$
- D_{ij} can become negative for $n > 2$
- multicomponent D_{ij} unrelated to binary counterpart
- R. Krishna and J.A. Wesselingh, Chem. Eng. Sci., 1997, 52, 861-911.

Maxwell-Stefan formulation at constant T, p

$$
\begin{aligned}
d_i &= \frac{x_i \nabla \mu_i}{RT} = \sum_{j=1, j\neq i}^{n} \frac{x_i x_j \left(u_j - u_i\right)}{Đ_{ij}} = \sum_{j=1, j\neq i}^{n} \frac{x_i J_j - x_j J_i}{c_t Đ_{ij}} \\
J_i &= u_i c_i = u_i x_i c_t \\
\sum_{i=1}^{n} x_i \nabla \mu_i &= 0
\end{aligned}
$$

- Gradient in chemical potential as driving force d_i
- n components, $n(n-1)/2$ MS diffusivities, $Đ_{ij} > 0$
- $Đ_{ij} = Đ_{ji}$ (Onsager's reciprocal relations)
- $Đ_{ij}$ is less composition dependent than Fick diffusivities
- Possibility to predict $Đ_{ij}$ using theory...

Diffusion coefficients depend on concentration!



Vignes equation in ternary systems

$$Đ_{ij} \approx \left(Đ_{ij}^{x_i \to 1}\right)^{x_i} \left(Đ_{ij}^{x_j \to 1}\right)^{x_j} \left(Đ_{ij}^{x_k \to 1}\right)^{x_k}$$

- Recommended in chemical engineering
- Is it any good?
- What about $Đ_{ij}^{x_k \to 1}$? Models for this in literature:

$$\begin{aligned}
\text{WK (1990)} \quad & Đ_{ij}^{x_k \to 1} = \sqrt{Đ_{ij}^{x_j \to 1} Đ_{ij}^{x_i \to 1}} \\
\text{KT (1991)} \quad & Đ_{ij}^{x_k \to 1} = \sqrt{Đ_{ik}^{x_k \to 1} Đ_{jk}^{x_k \to 1}} \\
\text{VKB (2005)} \quad & Đ_{ij}^{x_k \to 1} = \left(Đ_{ik}^{x_k \to 1}\right)^{\frac{x_i}{x_i + x_j}} \left(Đ_{jk}^{x_k \to 1}\right)^{\frac{x_j}{x_i + x_j}} \\
\text{DKB (2005)} \quad & Đ_{ij}^{x_k \to 1} = \frac{x_j}{x_i + x_j} Đ_{ik}^{x_k \to 1} + \frac{x_i}{x_i + x_j} Đ_{jk}^{x_k \to 1} \\
\text{RS (2007)} \quad & Đ_{ij}^{x_k \to 1} = \left(Đ_{ik}^{x_k \to 1} Đ_{jk}^{x_k \to 1} Đ_{ij}^{x_j \to 1} Đ_{ij}^{x_i \to 1}\right)^{1/4}
\end{aligned}$$

(Open?) Questions

- Is the quality of Vignes increased/decreased by a particular model choice for $Đ_{ij}^{x_k \to 1}$?
- Which of the predictive models for $Đ_{ij}^{x_k \to 1}$ is best for a certain system? (if any...)
- VKB and DKB suggest that $Đ_{ij}^{x_k \to 1}$ does not exist, $i.e.$ its value depends on the ratio x_i/x_j. Is this correct?

$$\begin{aligned}
\text{WK (1990)} \quad & Đ_{ij}^{x_k \to 1} = \sqrt{Đ_{ij}^{x_j \to 1} Đ_{ij}^{x_i \to 1}} \\
\text{KT (1991)} \quad & Đ_{ij}^{x_k \to 1} = \sqrt{Đ_{ik}^{x_k \to 1} Đ_{jk}^{x_k \to 1}} \\
\text{VKB (2005)} \quad & Đ_{ij}^{x_k \to 1} = \left(Đ_{ik}^{x_k \to 1}\right)^{\frac{x_i}{x_i + x_j}} \left(Đ_{jk}^{x_k \to 1}\right)^{\frac{x_j}{x_i + x_j}} \\
\text{DKB (2005)} \quad & Đ_{ij}^{x_k \to 1} = \frac{x_j}{x_i + x_j} Đ_{ik}^{x_k \to 1} + \frac{x_i}{x_i + x_j} Đ_{jk}^{x_k \to 1} \\
\text{RS (2007)} \quad & Đ_{ij}^{x_k \to 1} = (Đ_{ik}^{x_k \to 1} Đ_{jk}^{x_k \to 1} Đ_{ij}^{x_j \to 1} Đ_{ij}^{x_i \to 1})^{1/4}
\end{aligned}$$

Obtaining Maxwell-Stefan diffusivities from MD

$$\begin{aligned}\Lambda_{ij} &= \frac{1}{6N}\lim_{m\to\infty}\frac{1}{m\cdot\Delta t}\left\langle\left(\sum_{l=1}^{N_i}(r_{l,i}(t+m\cdot\Delta t)-r_{l,i}(t))\right)\times\right.\\ &\qquad\left.\left(\sum_{k=1}^{N_j}(r_{k,j}(t+m\cdot\Delta t)-r_{k,j}(t))\right)\right\rangle\\ &= \frac{1}{3N}\int_0^\infty dt\left\langle\sum_{l=1}^{N_i}v_{l,i}(0)\cdot\sum_{k=1}^{N_j}v_{k,j}(t)\right\rangle\end{aligned}$$

Note: $\Lambda_{ij}=\Lambda_{ji}$ (Onsager)

Krishna & Van Baten, Ind. Eng. Chem. Res., 2005, 44, 6939-6947.

Obtaining ternary Maxwell-Stefan diffusivities from MD

$$
\begin{aligned}
Đ_{12} &= \frac{A + (x_1 + x_3)\dfrac{B}{C}}{x_1 D} \\
A &= -\Lambda_{11}\Lambda_{23}x_2 - \Lambda_{12}x_3\Lambda_{21} + \Lambda_{11}x_3\Lambda_{22} - \Lambda_{11}x_3x_2\Lambda_{22} + \Lambda_{11}\Lambda_{23}x_2^2 - \Lambda_{11}x_3x_2\Lambda_{32} \\
&\quad +\Lambda_{11}\Lambda_{33}x_2^2 - \Lambda_{13}x_1\Lambda_{22} - x_1x_3\Lambda_{11}\Lambda_{22} + \Lambda_{13}\Lambda_{22}x_1^2 - x_1\Lambda_{31}x_3\Lambda_{22} + \Lambda_{33}x_1^2\Lambda_{22} \\
&\quad +\Lambda_{12}\Lambda_{23}x_1 + \Lambda_{12}x_3x_2\Lambda_{21} + \Lambda_{13}x_1x_2\Lambda_{22} + \Lambda_{12}x_3\Lambda_{31}x_2 + \Lambda_{13}x_2\Lambda_{21} - \Lambda_{13}x_2^2\Lambda_{21} \\
&\quad -\Lambda_{13}x_2^2\Lambda_{31} + x_1\Lambda_{12}x_3\Lambda_{21} - x_1^2\Lambda_{12}\Lambda_{23} + x_1\Lambda_{32}x_3\Lambda_{21} - x_1^2\Lambda_{32}\Lambda_{23} + \Lambda_{13}x_1x_2\Lambda_{32} \\
&\quad +x_1\Lambda_{11}\Lambda_{23}x_2 + x_1\Lambda_{31}\Lambda_{23}x_2 - \Lambda_{12}x_1\Lambda_{23}x_2 - \Lambda_{12}x_1\Lambda_{33}x_2 - x_1\Lambda_{13}x_2\Lambda_{21} \\
&\quad -x_1\Lambda_{33}x_2\Lambda_{21} \\
B &= \Lambda_{12}x_3 - \Lambda_{13}x_2 - x_1x_3\Lambda_{12} + x_1x_2\Lambda_{23} - x_1x_3\Lambda_{32} + x_1x_2\Lambda_{33} \\
C &= -\Lambda_{11}\Lambda_{23}x_2 - \Lambda_{12}\Lambda_{21}x_3 + x_3\Lambda_{11}\Lambda_{22} - x_2x_3\Lambda_{11}\Lambda_{22} + \Lambda_{11}\Lambda_{23}x_2^2 - x_2x_3\Lambda_{11}\Lambda_{32} \\
&\quad +\Lambda_{11}\Lambda_{33}x_2^2 - \Lambda_{13}\Lambda_{22}x_1 - x_1x_3\Lambda_{11}\Lambda_{22} + x_1^2\Lambda_{13}\Lambda_{22} - x_1x_3\Lambda_{31}\Lambda_{22} + x_1^2\Lambda_{22}\Lambda_{33} \\
&\quad +x_1\Lambda_{12}\Lambda_{23} + x_2x_3\Lambda_{12}\Lambda_{21} + x_1x_2\Lambda_{13}\Lambda_{22} + x_2x_3\Lambda_{12}\Lambda_{31} + x_2\Lambda_{13}\Lambda_{21} - x_2^2\Lambda_{13}\Lambda_{21} \\
&\quad -x_2^2\Lambda_{13}\Lambda_{31} + x_1x_3\Lambda_{12}\Lambda_{21} - x_1^2\Lambda_{12}\Lambda_{23} + x_1x_3\Lambda_{32}\Lambda_{21} - x_1^2\Lambda_{32}\Lambda_{23} + x_1x_2\Lambda_{13}\Lambda_{32} \\
&\quad +x_1x_2\Lambda_{11}\Lambda_{23} + x_1x_2\Lambda_{31}\Lambda_{23} - x_1x_2\Lambda_{12}\Lambda_{23} - x_1x_2\Lambda_{12}\Lambda_{33} - x_1x_2\Lambda_{13}\Lambda_{21} \\
&\quad -x_1x_2\Lambda_{33}\Lambda_{21} \\
D &= \Lambda_{22}x_3 - \Lambda_{23}x_2 - \Lambda_{22}x_3x_2 + \Lambda_{23}x_2^3 - x_2\Lambda_{12}x_3 + \Lambda_{13}x_2^2 - x_2\Lambda_{32}x_3 + \Lambda_{33}x_2^2
\end{aligned}
$$

Limit when $x_k \to 1$ (1)

$$
\begin{aligned}
\Lambda_{ii} &= \frac{1}{3N}\int_0^\infty dt \left\langle \sum_{l=1}^{N_i} v_{l,i}(0) \cdot \sum_{g=1}^{N_i} v_{g,i}(t) \right\rangle \\
&\approx \frac{N_i}{3N}\int_0^\infty dt \left\langle v_{i,1}(0) \cdot v_{i,1}(t) \right\rangle \\
&= x_i C_{ii} \\
\Lambda_{kk} &= \frac{1}{3N}\int_0^\infty dt \left\langle \sum_{l=1}^{N_k} v_{l,k}(0) \cdot \sum_{g=1}^{N_k} v_{g,k}(t) \right\rangle \\
&= \frac{1}{3N}\int_0^\infty dt \left\langle \sum_{l=1}^{N_k} v_{l,k}(0) \cdot v_{l,k}(t) \right\rangle + \frac{1}{3N}\int_0^\infty dt \left\langle \sum_{l=1}^{N_k} \sum_{g=1,g\neq l}^{N_k} v_{l,k}(0) \cdot v_{g,k}(t) \right\rangle \\
&\approx x_k C_{kk} + x_k^2 N C^\star_{kk} \\
\Lambda_{ij,j\neq i} &= \frac{1}{3N}\int_0^\infty dt \left\langle \sum_{l=1}^{N_i} v_{l,i}(0) \cdot \sum_{k=1}^{N_j} v_{k,j}(t) \right\rangle \\
&\approx \frac{N_i N_j}{3N}\int_0^\infty dt \left\langle v_{1,i}(0) \cdot v_{1,j}(t) \right\rangle \\
&= N x_i x_j C_{ij}
\end{aligned}
$$

Limit when $x_k \to 1$ (2)

Set $a = x_j/x_i$ and $x_k = 1 - x_i - x_j$, fill in the equations for Λ_{ii}, Λ_{jj}, Λ_{kk}, Λ_{ij}, Λ_{ik}, Λ_{jk} and take the limit $x_k \to 1$

Final result (after a lot of math):

Limit when $x_k \to 1$ (2)

Set $a = x_j/x_i$ and $x_k = 1 - x_i - x_j$, fill in the equations for Λ_{ii}, Λ_{jj}, Λ_{kk}, Λ_{ij}, Λ_{ik}, Λ_{jk} and take the limit $x_k \to 1$

Final result (after a lot of math):

$$\begin{aligned} Đ_{ij}^{x_k \to 1} &= \frac{D_{i,\mathrm{self}}^{x_k \to 1} \cdot D_{j,\mathrm{self}}^{x_k \to 1}}{D_{k,\mathrm{self}}^{x_k \to 1} + C_x} \\ C_x &= N\left(C_{ij} - C_{ik} - C_{jk} + C_{kk}^{\star}\right) \end{aligned}$$

which is independent of x_j/x_i !! (Note: C_x converges to a finite value when $N \to \infty$).

When cross-correlation are neglected:

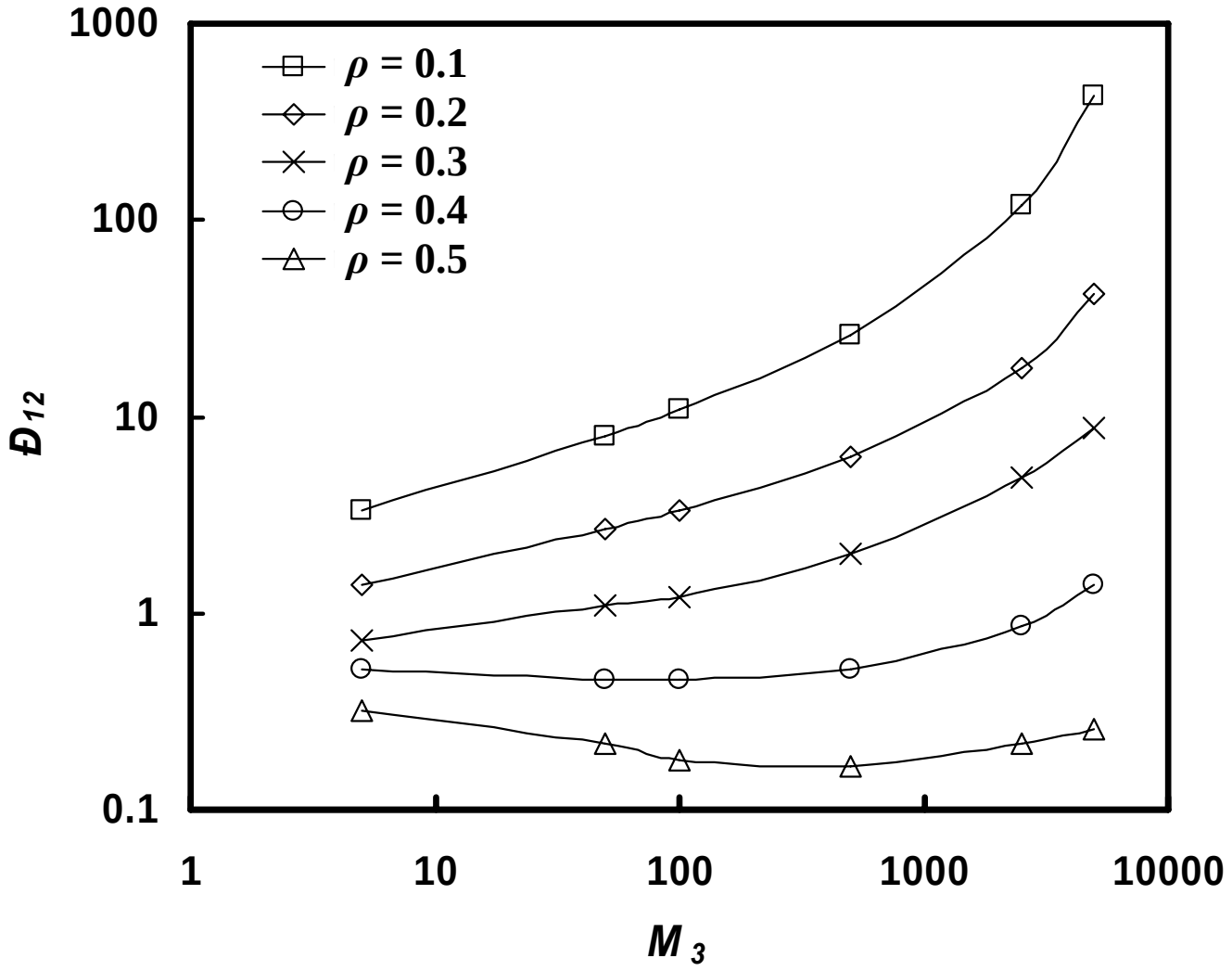
$$Đ_{ij}^{x_k \to 1} \approx \frac{D_{i,\mathrm{self}}^{x_k \to 1} \cdot D_{j,\mathrm{self}}^{x_k \to 1}}{D_{k,\mathrm{self}}^{x_k \to 1}}$$

Ternary system of WCA particles that only differ in mass

	MS diffusivity $Đ_{12}^{x_3 \to 1}$						
	incl. C_x	$C_x = 0$	WK	KT	VKB	DKB	RS
Prediction	1.401	1.441	1.296	0.952	0.952	0.952	1.111
MD [b]	1.411	1.411	1.411	1.411	1.411	1.411	1.411
AD [a]	**1%**	**2%**	**8%**	**32%**	**32%**	**32%**	**21%**
Prediction	0.310	0.315	0.390	0.248	0.248	0.248	0.311
MD [c]	0.318	0.318	0.318	0.318	0.318	0.318	0.318
AD [a]	**2%**	**1%**	**23%**	**22%**	**22%**	**22%**	**2%**
Prediction	3.344	3.288	1.296	0.682	0.682	0.683	0.940
MD [d]	3.348	3.348	3.348	3.348	3.348	3.348	3.348
AD [a]	**0%**	**2%**	**61%**	**80%**	**80%**	**80%**	**72%**
Prediction	0.172	0.161	0.389	0.101	0.101	0.101	0.198
MD [e]	0.172	0.172	0.172	0.172	0.172	0.172	0.172
AD [a]	**0%**	**7%**	**126%**	**42%**	**42%**	**42%**	**15%**

[a] absolute difference normalized with corresponding value from MD simulations
[b] $\rho = 0.2$; $M_1 = 1$; $M_2 = 1.5$; $M_3 = 5$; $x_1/x_2 = 1$; $x_3 = 0.95$; $T = 2$
[c] $\rho = 0.5$; $M_1 = 1$; $M_2 = 1.5$; $M_3 = 5$; $x_1/x_2 = 1$; $x_3 = 0.95$; $T = 2$
[d] $\rho = 0.2$; $M_1 = 1$; $M_2 = 1.5$; $M_3 = 100$; $x_1/x_2 = 1$; $x_3 = 0.95$; $T = 2$
[e] $\rho = 0.5$; $M_1 = 1$; $M_2 = 1.5$; $M_3 = 100$; $x_1/x_2 = 1$; $x_3 = 0.95$; $T = 2$

Increasing the mass of the solvent (M_3)



$$Đ_{ij}^{x_k \to 1} \approx \frac{D_{i,\mathrm{self}}^{x_k \to 1} \cdot D_{j,\mathrm{self}}^{x_k \to 1}}{D_{k,\mathrm{self}}^{x_k \to 1}}$$

(1) n-hexane / (2) cyclohexane / (3) toluene

	MS Diffusivity/$(10^{-9}\ \mathrm{m^2 s^{-1}})$				
	MD simulation	Prediction of $Đ_{ij}^{x_k \to 1}$			
	$Đ_{23}$	incl. C_x	AD[a]	$C_x = 0$	AD[a]
$x_1 \to 1$[b]	4.07	4.12	**1%**	3.78	**7%**
	$Đ_{13}$	incl. C_x	AD[a]	$C_x = 0$	AD[a]
$x_2 \to 1$[c]	2.19	2.21	**1%**	2.69	**23%**
	$Đ_{12}$	incl. C_x	AD[a]	$C_x = 0$	AD[a]
$x_3 \to 1$[d]	2.99	2.93	**2%**	2.82	**6%**

[a] absolute difference normalized with corresponding value from MD simulations
[b] 598 n-hexane molecules; 1 cyclohexane molecule; 1 toluene molecule
[c] 1 n-hexane molecule; 598 cyclohexane molecules; 1 toluene molecule
[d] 1 n-hexane molecule; 1 cyclohexane molecule; 598 toluene molecules

298K, 1 atm.

(1) ethanol / (2) methanol / (3) water

	$Đ_{ij}^{x_k \to 1}/(10^{-9}\ \mathrm{m^2 s^{-1}})$						
	incl. C_x	$C_x = 0$	WK	KT	VKB	DKB	RS
Prediction of $Đ_{23}$	2.68	1.57	2.07	1.25	1.25	1.32	1.61
MD [b]	2.68	2.68	2.68	2.68	2.68	2.68	2.68
AD [a]	**0%**	**41%**	**23%**	**53%**	**53%**	**51%**	**40%**
Prediction of $Đ_{13}$	3.17	2.07	1.20	2.04	2.04	2.06	1.56
MD [c]	3.24	3.24	3.24	3.24	3.24	3.24	3.24
AD [a]	**2%**	**36%**	**63%**	**37%**	**37%**	**37%**	**52%**
Prediction of $Đ_{12}$	5.01	1.06	1.78	1.72	1.72	1.73	1.75
MD [d]	4.76	4.76	4.76	4.76	4.76	4.76	4.76
AD [a]	**5%**	**78%**	**63%**	**64%**	**64%**	**64%**	**63%**

[a] absolute difference normalized with corresponding result from MD simulations

[b] 168 ethanol molecules; 1 methanol molecule; 1 water molecule

[c] 1 ethanol molecule; 248 methanol molecules; 1 water molecule

[d] 1 ethanol molecule; 1 methanol molecule; 598 water molecules

298K, 1 atm. Lennard-Jones+electrostatics (Ewald summation)

Consistent multicomponent Darken

Darken equation for a binary system (1945)

$$Đ_{ij} = x_i D_{j,\mathrm{self}} + x_j D_{i,\mathrm{self}}$$

Generalized Darken for multicomponent system (empirical)

$$Đ_{ij} = \frac{x_i}{x_i + x_j} D_{j,\mathrm{self}} + \frac{x_j}{x_i + x_j} D_{i,\mathrm{self}}$$

Multicomponent Darken (Ind. Eng. Chem. Res., 2011, 50, 10350-10358.)

$$Đ_{ij} = D_{i,\mathrm{self}} D_{j,\mathrm{self}} \sum_{i=1}^{n} \frac{x_i}{D_{i,\mathrm{self}}}$$

- derived by assuming that velocity cross-correlations are much smaller than velocity self-correlations
- for $n = 2$, multicomponent Darken reduces to binary Darken
- for a ternary system for $x_k \to 1$, our equation for $Đ_{ij}^{x_k \to 1}$ is recovered

Converting Fick and Maxwell-Stefan diffusivities

$$[D_{ij}^{\mathrm{Fick}}] = [B_{ij}]^{-1}[\Gamma_{ij}]$$

$$B_{ii} = \frac{x_i}{Đ_{in}} + \sum_{j=1, j\neq i}^{n} \frac{x_j}{Đ_{ij}} \qquad \text{with } i = 1, \cdots, (n-1)$$

$$B_{ij} = -x_i \left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}} \right) \qquad \text{with } i, j = 1, \cdots, (n-1) \quad i \neq j$$

$$\Gamma_{ij} = \delta_{ij} + x_i \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{T,p,\Sigma}$$

Note: molar reference frame for $[D_{ij}^{\mathrm{Fick}}]$

Obtaining Fick diffusivities (1)

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{p,T} = -\frac{c_2\left(G_{22}+G_{11}-2G_{12}\right)}{1+c_2 x_1\left(G_{22}+G_{11}-2G_{12}\right)}$$

$$G_{\alpha\gamma} = v\frac{\langle N_\alpha N_\gamma\rangle - \langle N_\alpha\rangle\langle N_\gamma\rangle}{\langle N_\alpha\rangle\langle N_\gamma\rangle} - \frac{\delta_{\alpha\gamma}}{c_\alpha}$$

$$= 4\pi\int_0^\infty \left[g_{\alpha\gamma}^{\mu VT}(r)-1\right] r^2 dr$$

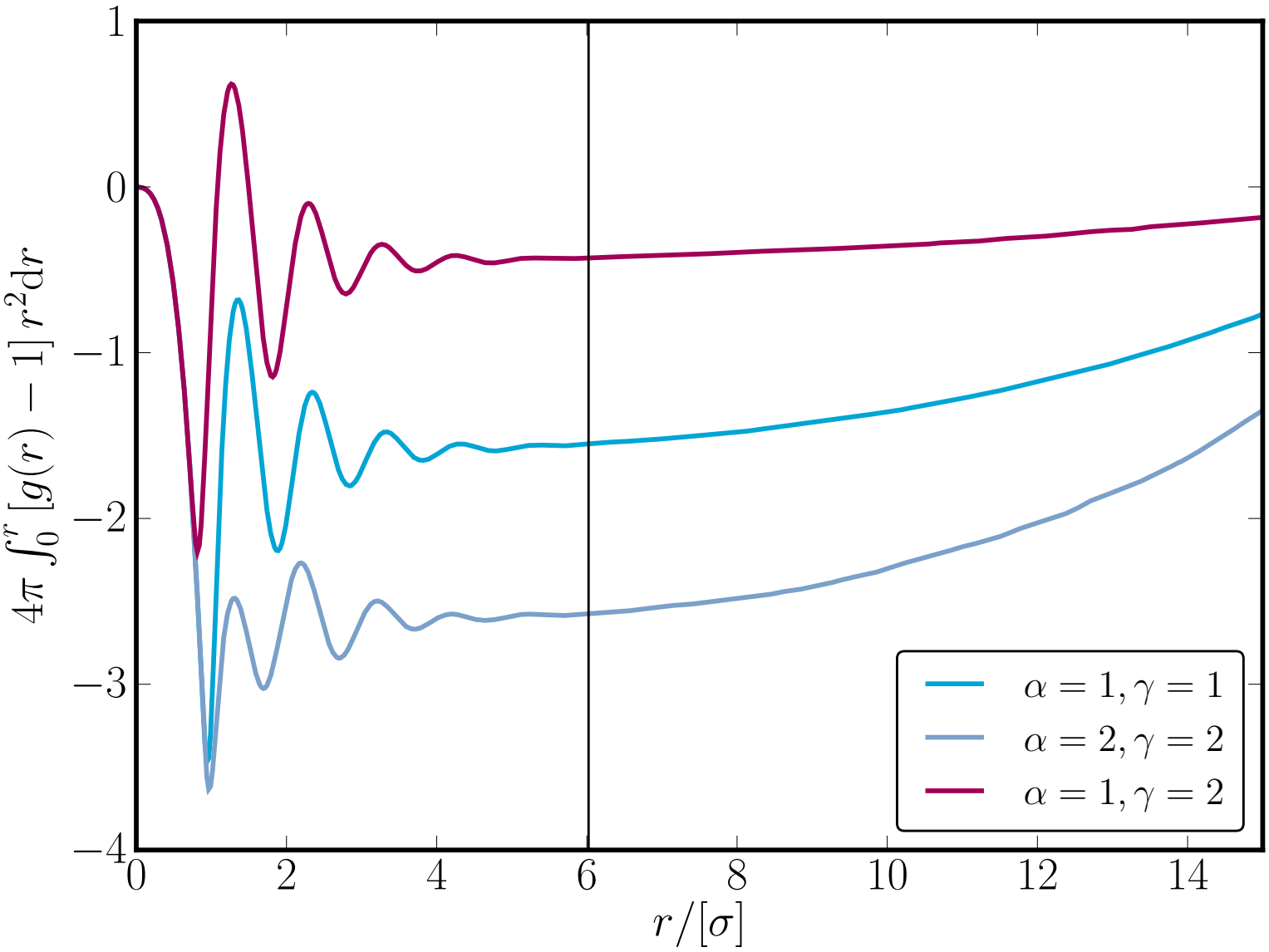
$$\approx 4\pi\int_0^\infty \left[g_{\alpha\gamma}^{NVT}(r)-1\right] r^2 dr$$

with $c_\alpha = \langle N_\alpha\rangle / v$ and $\langle\cdots\rangle$ denotes an average in the μVT ensemble

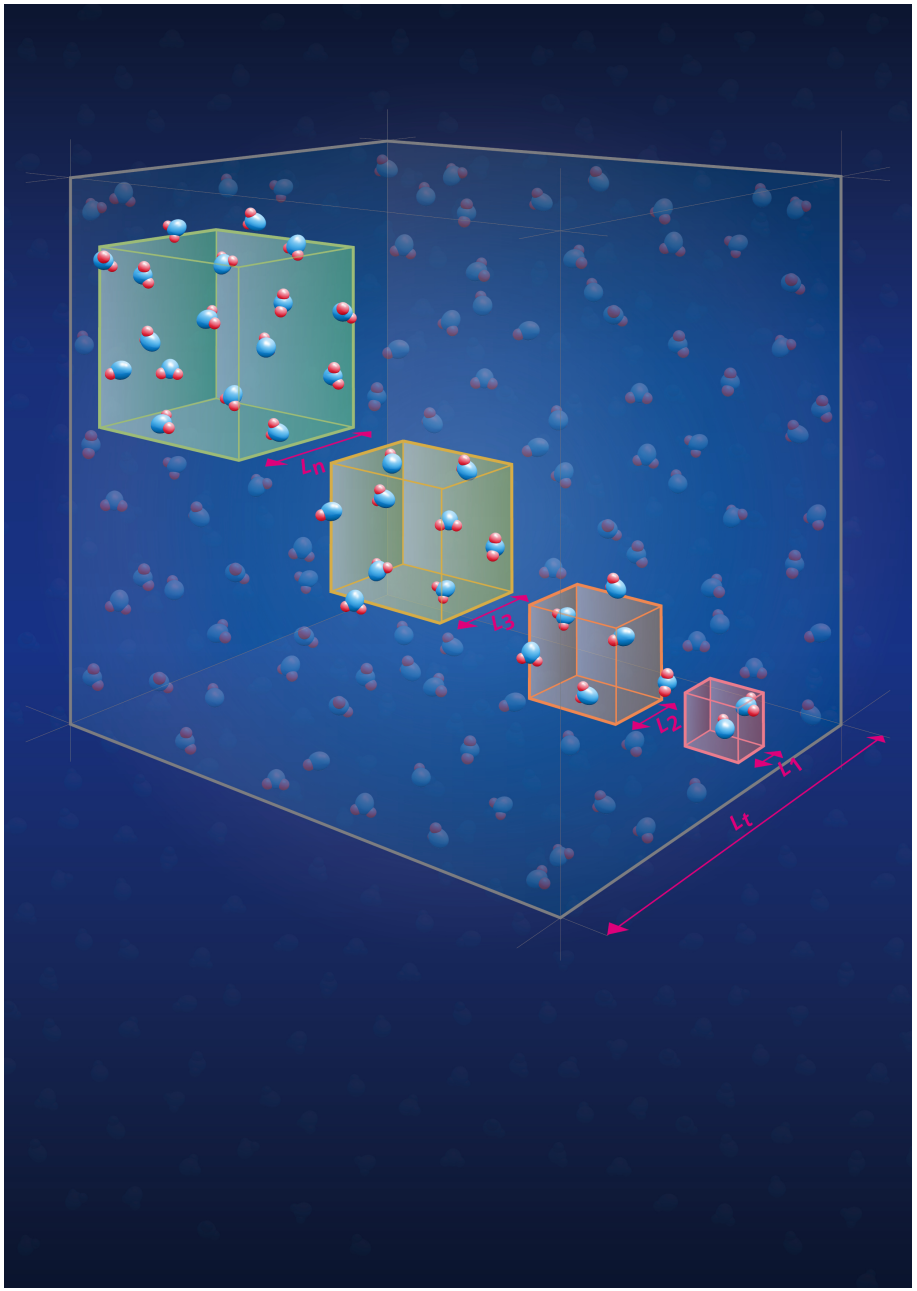
$G_{\alpha\gamma}$: Total Correlation Function Integral (TCFI)

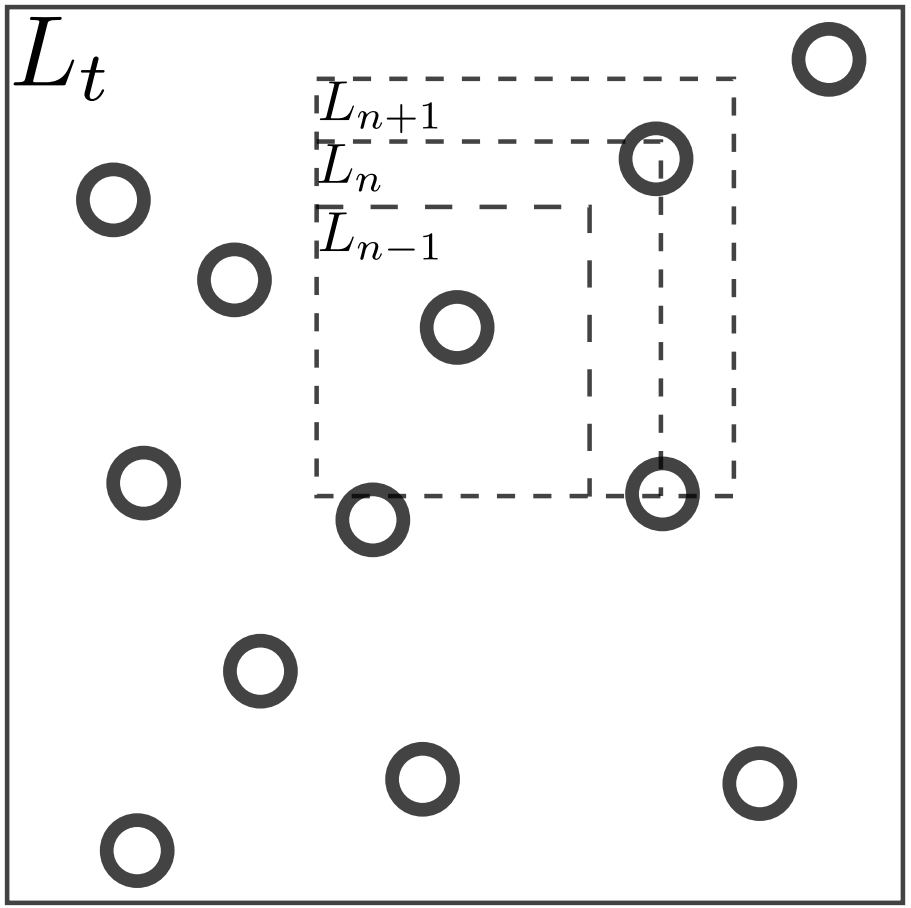
Kirkwood and Buff, J. Chem. Phys., 1951, 19, 774-778.

Obtaining Fick diffusivities (2)

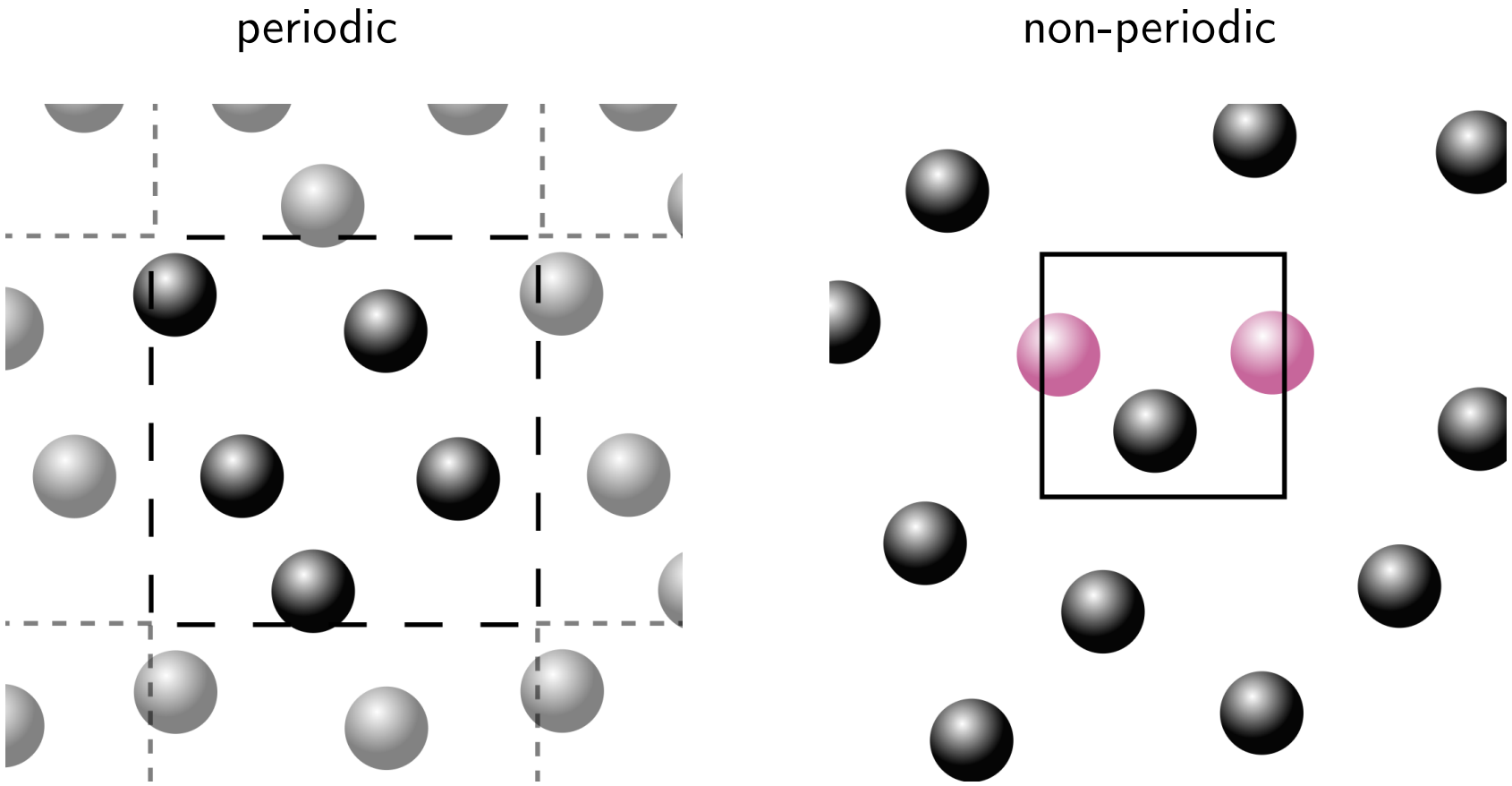


Obtaining Fick diffusivities (3)

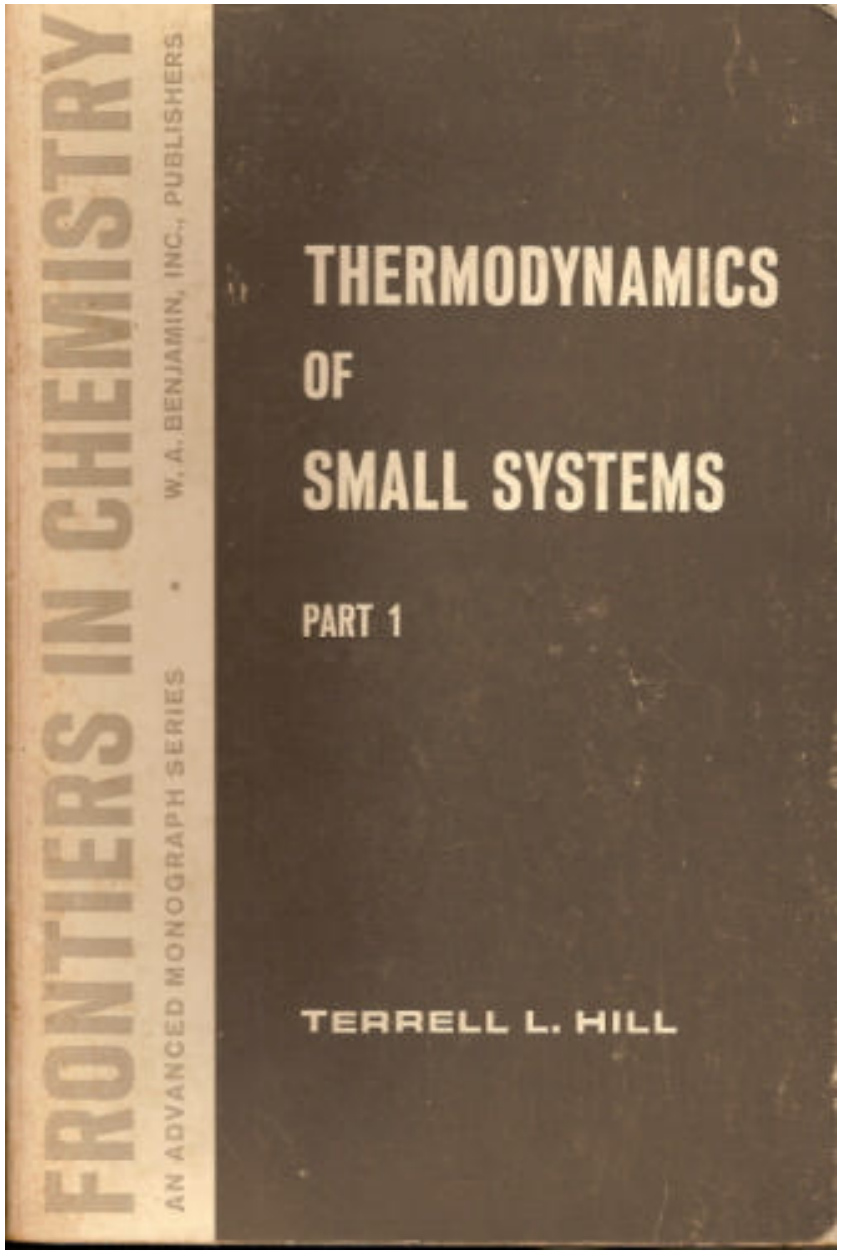




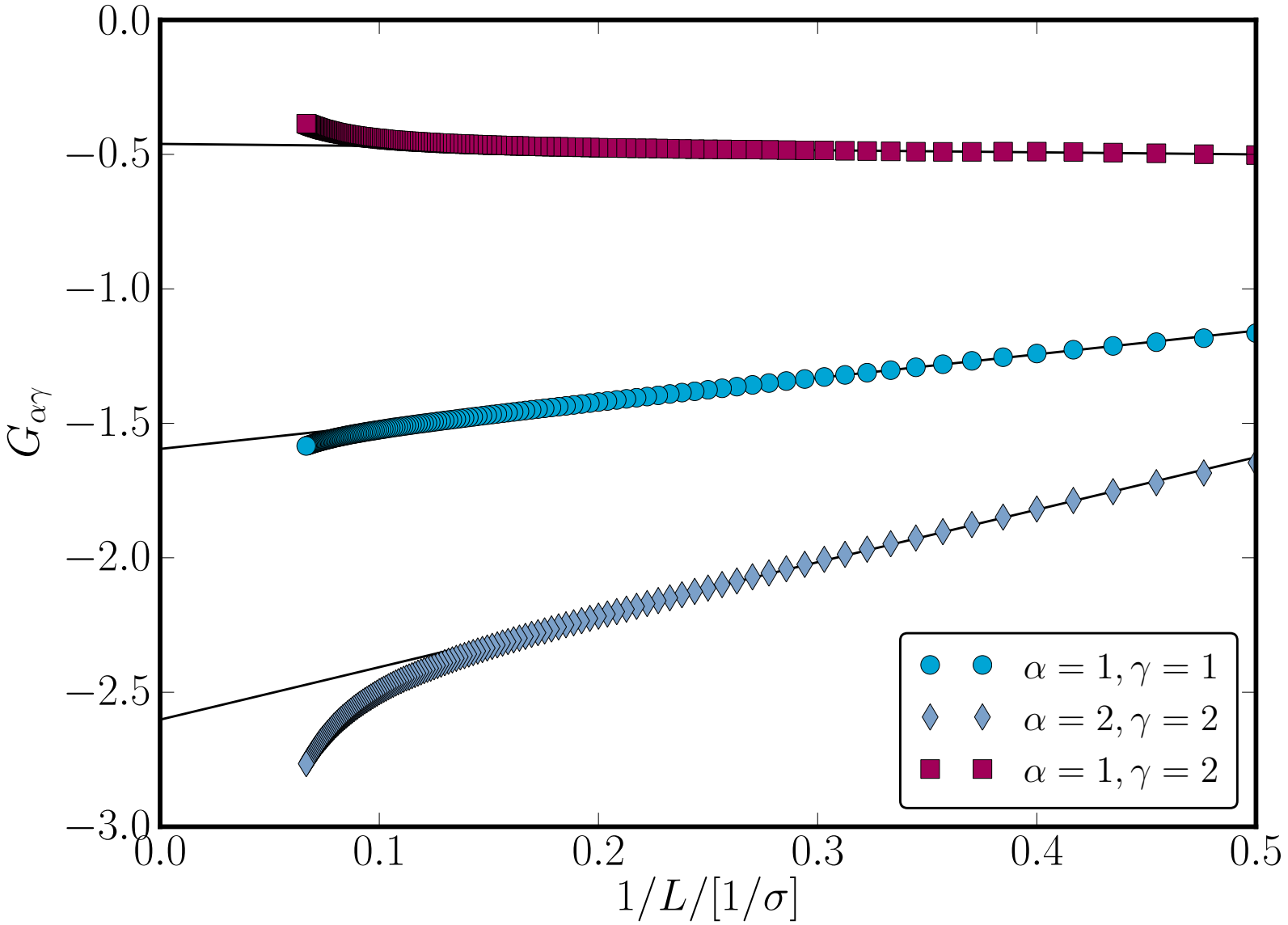
Obtaining Fick diffusivities (4)



Obtaining Fick diffusivities (5)



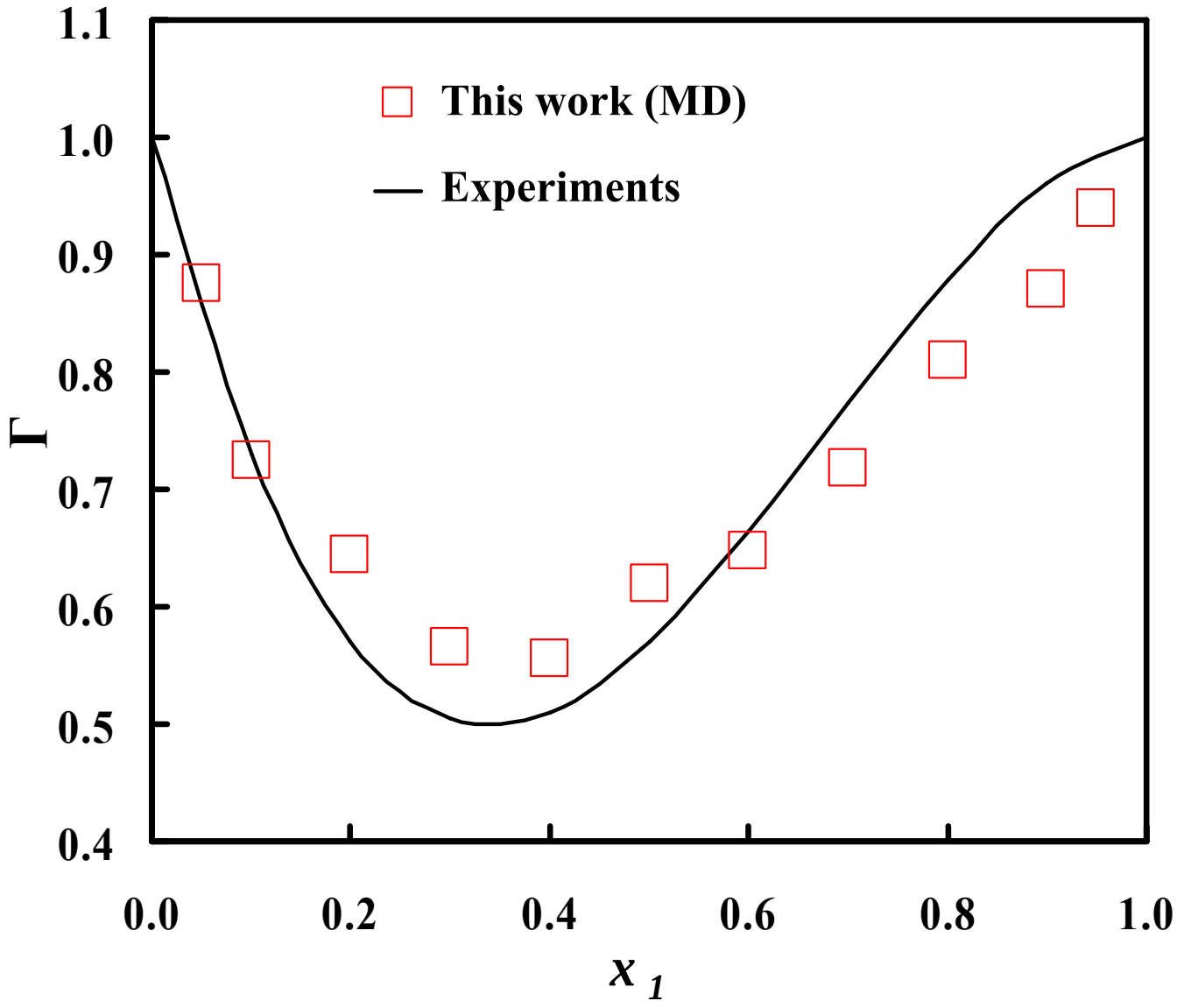
Obtaining Fick diffusivities (6)



Obtaining Fick diffusivities (7)

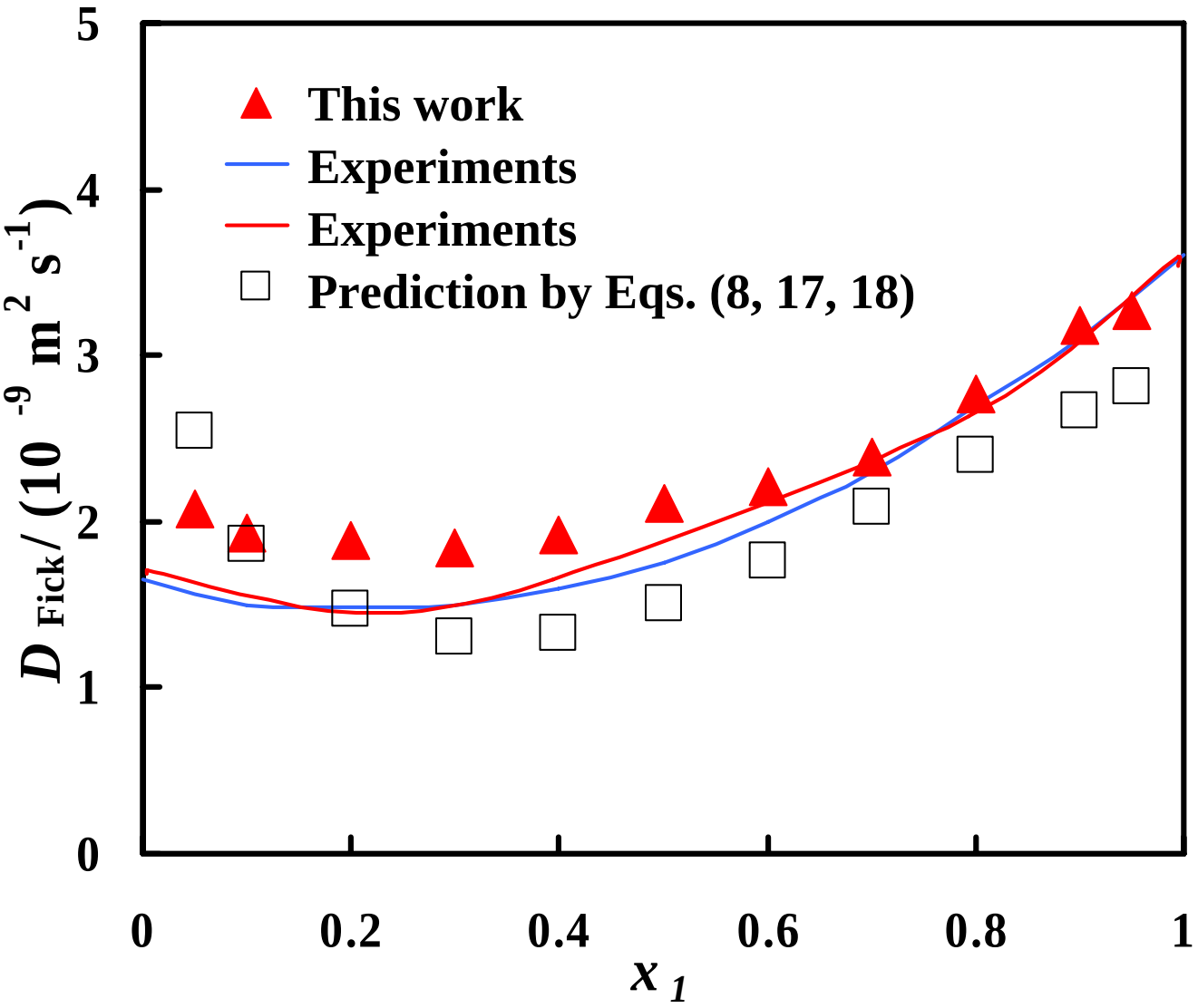
$L_t/[\sigma]$	$\alpha\delta$	$R/[\sigma]$	from $g(r)$	new method
	11		-0.977	-1.601
10	22	4.503	-1.633	-2.686
	12		-0.275	-0.440
	11		-1.508	-1.594
20	22	5.000	-2.456	-2.601
	12		-0.429	-0.464
	11		-1.552	-1.600
30	22	6.023	-2.577	-2.602
	12		-0.428	-0.461
	11		-1.574	-1.600
40	22	6.027	-2.555	-2.621
	12		-0.455	-0.463

Acetone-tetrachloromethane (1)



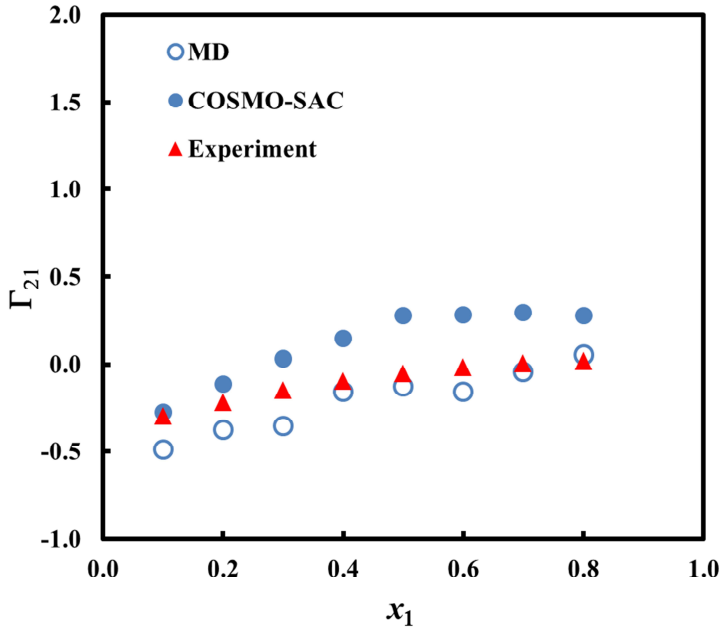
298K, 1atm

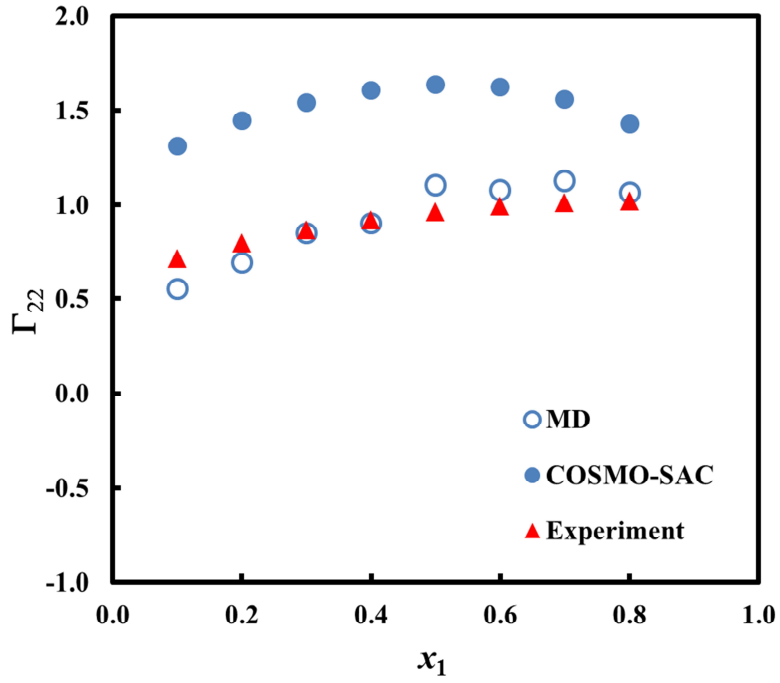
Acetone-tetrachloromethane (2)



298K, 1atm

Chloroform(1)-Acetone(2)-Methanol(3) ($x_2 = x_3$)





298K, 1atm

Conclusions

- Transport diffusion coefficients depend on concentration
- Molecular Dynamics and theory are useful tools for developing predictive models for calculating transport diffusivities
- A consistent multicomponent Darken equation was developed
- A new way was found for computing Γ_{ij} from Molecular Dynamics simulations, thereby bridging the gap between experiments and simulations