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Prediction of concentration-dependent self-diffusion coefficients in binary liquid mixtures: The missing link for Darken-based models

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Abstract

Mutual diffusion coefficients can be successfully predicted with models based on the Darken equation. However, Darken-based models require concentration-dependent self-diffusion coefficients which are rarely available. In this work, we present a predictive model for concentration-dependent self-diffusion coefficients (also called tracer diffusion coefficients) in non-ideal binary liquid mixtures. The model is derived from Molecular Dynamics simulation data of Lennard-Jones systems. A strong correlation between non-ideal diffusion effects and the thermodynamic factor is observed. We extend the model by McCarty and Mason (Phys. Fluids. 1960, 3, 908-922) for ideal binary gas

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mixtures to predict the concentration-dependent self-diffusion coefficients in non-ideal binary liquid mixtures. Our new model is a function of the thermodynamic factor and the self-diffusion coefficients at infinite dilution and of the pure substances which are readily available. We validate our model with experimental data of 9 systems. For both Lennard-Jones systems and experimental data, the accuracy of the predicted self-diffusion coefficients is improved by a factor 2 compared to the correlation of McCarty and Mason. Thus, our new model significantly expands the practical applicability of Darken-based models for the prediction of mutual diffusion coefficients.

1 Introduction

Diffusion in liquids plays an important role in many industrial and environmental processes.[1] Engineers are in need of precise diffusion process calculations to design, e.g., separation processes and chemical reactors. The accurate quantitative description of diffusion processes has been a challenge to scientists for decades.[2,3] There is still a continuing demand for diffusion coefficients as input parameters to these models.[4]

Although experimental methods are continuously improving,[5–10] the measurement of diffusion coefficients in liquids is usually time-consuming and expensive.[11,12]

Molecular Dynamics (MD) simulations are a powerful tool to complement or even substitute diffusion experiments.[13–15] However, MD simulations are still computationally too expensive to be performed in the framework of process simulations. Therefore, predictive models for diffusion coefficients are needed.[11,16–18] The aim is to reduce the required data to a minimal amount, e.g., to viscosities or diffusion coefficients at infinite dilution.

Most practical applications require the knowledge of *mutual diffusion coefficients*, which describe the net flow of molecules due to a driving force. Numerous models have been proposed to predict the concentration dependence of mutual diffusion coefficients in liquids.[11,16–20] Within these models, two main classes can be identified:

The first class of models is based on the Vignes equation[21]

$$Đ_{12} = \left(Đ_{12}^{x_1 \to 1}\right)^{x_1} \left(Đ_{12}^{x_2 \to 1}\right)^{x_2}. \tag{1}$$

Here, $Đ_{12}$ is the (mutual) Maxwell-Stefan (MS) diffusion coefficient, x_1 and x_2 are the mole fractions of components 1 and 2, and $Đ_{12}^{x_1 \to 1}$ and $Đ_{12}^{x_2 \to 1}$ are the MS diffusion coefficients at infinite dilution. The Vignes equation is very popular since it only requires diffusion coefficients at infinite dilution as input for which many predictive models are available such as e.g. the Wilke-Change equation.[19] The Vignes equation is purely empirical and applicable to binary systems only. However, extensions of the Vignes equation to multicomponent mixtures have been proposed.[16,18]

The second class of models is based on the Darken equation[22]

$$Đ_{12} = Đ_{\text{Darken}} = x_2 D_{1,\text{self}} + x_1 D_{2,\text{self}}. \tag{2}$$

Here, $D_{1,\text{self}}$ and $D_{2,\text{self}}$ are the concentration-dependent *self-diffusion coefficients* (also called tracer diffusion coefficients) of components 1 and 2 in the mixture, which describe the mean-square displacements of individual molecules in a mixture. The Darken equation has been extended to multicomponent mixtures by Liu et al.[18,23] In contrast to the Vignes equation (Equation 1), the Darken equation has a physical basis and can be derived from statistical-mechanical theory when velocity crosscorrelations between the molecules of a mixture are neglected, i.e. when the molecules in the mixture move independently and not in groups or clusters.[18] Hence, the Darken equation is suitable for ideal mixtures, but not for strongly non-ideal mixtures.

A modified Darken equation for non-ideal binary mixtures has therefore been proposed by D'Agostino et al.[24] and Moggridge[25] which is based on critical point scaling laws:[26–29]

$$Đ_{12} = Đ_{\text{Darken}} \Gamma^{-0.36}. \tag{3}$$

Here, the Darken equation is corrected by a power function of the thermodynamic factor Γ, which is a measure for the nonideality of the system (cf. Equation 8).[3] In the rest of the manuscript, Equation 3 is called the "Moggridge equation". The Moggridge equation has been tested and successfully validated for a wide range of non-ideal liquid mixtures.[15,24,25,30] The Moggridge equation is not applicable to mixtures with dimerising components. Moggridge[31] proposed a further modification of Equation 3 for mixtures with dimerising components. Zhu et al.[32] introduced local mole fractions into the Moggridge equation. Thereby, mixtures with and without dimerising species could be successfully described. Recently, Allie-Ebrahim et al.[33] suggested an extension of the Moggridge equation to multicomponent systems.

Despite its sound physical background, the Darken equation (and thereby the Moggridge equation) is generally seen as "of little practical use due to the fact that it relies on the self-diffusion coefficients [$D_{i,\mathrm{self}}$] in the mixture, which are rarely available".[34] To avoid the use of $D_{i,\mathrm{self}}$, modifications of the Darken equation have been proposed which use self-diffusion coefficients at infinite dilution $D_{i,\mathrm{self}}^{x_{j\neq i}\to 1} = D_{ij}^{x_{j\neq i}\to 1} = D_{12}^{\infty}$,[35] include additional, system-dependent modification factors,[36] or incorporate the shear viscosity,[37,38] to name a few. Similar modifications have been applied to the Vignes equation to extend the applicability to a wider range of non-ideal systems.[39] However, the applicabilities of the (modified) Vignes equations and of those modified Darken equations that avoid the use of $D_{i,\mathrm{self}}$ are very case specific.[3,19] It was concluded that "no single correlation [that avoids the use of concentration-dependent self-diffusion coefficients $D_{i,\mathrm{self}}$] is always satisfactory for estimating the concentration effect on liquid diffusion coefficients".[19] Therefore, the concentration-dependent self-diffusion coefficients should preferentially not be replaced in the Darken-based models.

Thus, reliable predictions of concentration-dependent *self-diffusion coefficients* $D_{i,\mathrm{self}}$ are needed. Existing predictive models for $D_{i,\mathrm{self}}$ predict $D_{i,\mathrm{self}}$ from the self-diffusion coefficients

at infinite dilution, $D_{i,\text{self}}^{x_j \to 1}$. Carman and Stein[40] proposed the semi-empirical relation

$$D_{i,\text{self,pred}} = \frac{D_{i,\text{self}}^{x_j \to 1} \eta^{x_j \to 1}}{\eta} \tag{4}$$

for binary systems, where $D_{i,\text{self,pred}}$ is the predicted value of $D_{i,\text{self}}$, $\eta^{x_j \to 1}$ is the viscosity of pure component j, and η is the viscosity of the mixture. Equation 4 is based on the Stokes-Einstein equation[19] and works well for ideal mixtures.[40] For non-ideal mixtures, large deviations occur.[15]

For non-ideal mixtures, Krishna and van Baten[41] suggest the empirical relation

$$D_{i,\text{self,pred}} = \sum_{j=1}^{n} w_j D_{i,\text{self}}^{x_j \to 1}, \tag{5}$$

where w_j is the mass fraction of component j. Equation 5 was successfully tested for linear alkanes[41] and mixtures with thermodynamic factors $0.55 \leq \Gamma \leq 1$.[15] For strongly non-ideal mixtures with thermodynamic factors $\Gamma < 0.55$, large deviations were observed.[15]

Based on derivations of Curtiss and Hirschfelder[42] and Hirschfelder and Curtiss,[43] McCarty and Mason[44] and Miller and Carman[45] derived the relation

$$\frac{1}{D_{i,\text{self,pred}}} = \frac{x_1}{D_{i,\text{self}}^{x_1 \to 1}} + \frac{x_2}{D_{i,\text{self}}^{x_2 \to 1}}, \quad i = 1, 2. \tag{6}$$

for binary gas mixtures. In the rest of the manuscript, Equation 6 will be called the "McCarty-Mason equation". The McCarty-Mason equation is based on the assumption of an approximately constant mutual diffusion coefficient, which is an often valid assumption for gases. It is exact in the limit of infinite dilution.[18] McCarty and Mason[44] and Miller and Carman[45] tested the McCarty-Mason equation successfully with data from gas diffusion experiments. Liu et al.[18] proposed the use of the McCarty-Mason equation for weakly non-ideal liquids. Satisfying predictions of self-diffusion coefficients in weakly non-ideal liquids were observed.[15,18,23] However, Equation 6 performs poorly for strongly non-ideal mixtures.[15]

Overall, the predictive models for concentration-dependent self diffusion coefficients (Eqs. 4, 5, and 6) work well for approximately ideal mixtures, but there is a need for predictive equations for non-ideal mixtures. For *mutual* diffusion coefficients, the successful performance of the Moggridge equation (Equation 3) shows that the inclusion of a function of the thermodynamic factor Γ into the ideal *mutual* diffusion equation (the Darken Equation 2) can be a sufficient method to take nonidealities into account. The question arises whether it is also possible to correct the ideal *self*-diffusion equation (the McCarty-Mason Equation 6) with a function of the thermodynamic factor Γ to expand its applicability to non-ideal mixtures.

In this work, we study the concentration-dependence of mutual and self-diffusion coefficients in binary non-ideal liquid mixtures. We investigate the correlation of non-ideal diffusion effects with the thermodynamic factor. In Section 2, we motivate our analysis from a theoretical point of view. Since experimental data rarely provide a full set of transport data and thermodynamic properties, we use Molecular Dynamics (MD) simulations as the basis for our analysis (Section 3). In Section 4.1, we assess the performance of the Moggridge equation (Equation 3) for the prediction of mutual diffusion coefficients. In Section 4.2.1, we analyze the non-ideal behavior of self-diffusion coefficients and derive an improved model for the prediction of self-diffusion coefficients in strongly non-ideal binary liquid mixtures. In Section 4.2.2, the improved model is tested and validated with experimental data of molecular systems. Conclusions of this study are drawn in Section 5.

2 Theory and Method

Commonly, two approaches are used to describe mutual diffusion: Fick's approach and the Maxwell-Stefan (MS) approach.[3,46] Fick's approach is phenomenological and requires the knowledge of Fick diffusion coefficients D_{12} and of concentration gradients. It is therefore often used for practical applications. The MS approach is physically motivated and can be derived from irreversible thermodynamics.[3,47] It requires the knowledge of MS diffusion

coefficients $Đ_{12}$ and of chemical potential gradients. Hence, the MS approach separates thermodynamic properties and transport properties. It is therefore often used for predictive modeling of diffusion coefficients.

Since both Fick's and the MS approach describe the same phenomenon, they are linked to each other. For a binary mixture, we have

$$D_{12} = Đ_{12}\Gamma \tag{7}$$

holds, where Γ is the thermodynamic factor. The MS diffusion coefficient $Đ_{12}$ describes the molecular friction forces whereas the thermodynamic factor Γ contains the thermodynamic information.

For a binary mixture, the thermodynamic factor Γ is defined as[3]

$$\Gamma = 1 + x_1 \left.\frac{\partial \ln \gamma_1}{\partial x_1}\right|_{T,p,\Sigma} = 1 + x_1 \left.\left(\frac{\partial \ln \gamma_1}{\partial x_1} - \frac{\partial \ln \gamma_1}{\partial x_2}\right)\right|_{T,p}. \tag{8}$$

Here, γ_1 is the activity coefficient of component 1, T and p denote temperature and pressure, respectively, and Σ indicates that the closing condition $\sum_i x_i = 1$ has to be considered. For ideal mixtures and pure substances, $\Gamma = 1$ holds by definition. Thus, MS diffusion coefficients and Fick diffusion coefficients are equal for ideal mixtures, pure substances, and at infinite dilution. Mixtures with a thermodynamic factor $0 < \Gamma < 1$ favor interactions between the same species over interactions between different species. If Γ approaches zero, the mixture is approaching phase separation. Mixtures with $\Gamma > 1$ exhibit associating behavior.

The thermodynamic factor Γ can be calculated from excess enthalpy models[3] or equations of state.[41] In molecular simulations, the thermodynamic factor can be calculated from Kirkwood-Buff integrals[48] or the permuted Widom test particle insertion method.[49] In this work, the thermodynamic factors of LJ systems are calculated from Kirkwood-Buff integrals G_{ij}:[13]

$$\Gamma = \left(1 + \frac{1}{V} x_1 x_2 N \left(G_{11} + G_{22} - 2G_{12}\right)\right)^{-1}. \tag{9}$$

Here, V is the volume of the simulation box and N is the total number of particles. For details, the reader is referred to Milzetti et al.,[50] Ben-Naim,[51] and Jamali et al.[52]

The MS diffusion coefficient can be expressed by velocity correlation functions. For a binary mixture, the MS diffusivity $Đ_{12}$ equals[23]

$$Đ_{12} = \underbrace{x_2 D_{1,\text{self}} + x_1 D_{2,\text{self}}}_{Đ_{\text{Darken}}} + \underbrace{x_1 x_2 N (CC_{11} + CC_{22} - 2CC_{12})}_{Đ_{\text{Cross}}}. \tag{10}$$

The MS diffusion coefficient $Đ_{12}$ is composed of two parts: An (ideal) Darken diffusion coefficient $Đ_{\text{Darken}}$ containing the self-diffusion coefficients $D_{i,\text{self}}$ (which are velocity autocorrelations), and a non-ideal diffusion coefficient $Đ_{\text{Cross}}$ containing the velocity crosscorrelations CC_{ij} between different particles of components i and j. For approximately ideal mixtures with weak molecular interactions, the velocity crosscorrelations CC_{ij} are negligible compared to the self-diffusion coefficients $D_{i,\text{self}}$ and the MS diffusion coefficient is approximately the Darken diffusion coefficient: $Đ_{12} \approx Đ_{\text{Darken}}$. For non-ideal mixtures with strong molecular interactions, the non-ideal diffusion coefficient $Đ_{\text{Cross}}$ can be in the same order of magnitude as the Darken diffusion coefficient $Đ_{\text{Darken}}$. Thus, consideration of $Đ_{\text{Cross}}$ is essential for non-ideal mixtures.

A number of works have studied the concentration dependence of velocity crosscorrelations CC_{ij}.[53–64] Weingärtner[54] observed that velocity crosscorrelations CC_{ij} show a similar concentration-dependence as Kirkwood-Buff coefficients G_{ij}. However, a derivation of a relationship between velocity crosscorrelations CC_{ij} and the thermodynamic factor Γ is not straight-forward and no conclusive answer was found. Still, it is interesting to note that Weingärtner's observation in fact suggests a connection between the non-ideal diffusion coefficient $Đ_{\text{Cross}}$ and the thermodynamic factor Γ: A comparison of Equation 9 and Equation 10 reveals a structural similarity in the formulations of $Đ_{\text{Cross}}$ and Γ. Similarly, the Moggridge equation (Equation 3) also suggests a correlation between the relative nonideality $Đ_{\text{Cross}}/Đ_{\text{Darken}}$ and Γ: insertion of the Moggridge equation (Equation 3) into Equation 10

leads to

$$\frac{Đ_{\mathrm{Cross}}}{Đ_{\mathrm{Darken}}} = \frac{Đ_{12} - Đ_{\mathrm{Darken}}}{Đ_{\mathrm{Darken}}} \tag{11}$$

$$= \frac{Đ_{12}}{Đ_{\mathrm{Darken}}} - 1 \tag{12}$$

$$= \Gamma^{-0.36} - 1. \tag{13}$$

Thus, the Moggridge equation (Equation 3) in fact relates the non-ideal diffusion coefficient $Đ_{\mathrm{Cross}}$ to the ideal Darken diffusion coefficient $Đ_{\mathrm{Darken}}$ and the thermodynamic factor Γ.

The question arises whether the relation between non-ideal diffusion effects and the thermodynamic factor can also be observed for self-diffusion coefficients. The McCarty-Mason equation (Equation 6) resembles the ideal mixing rule for concentration-dependent self-diffusion coefficients. In an analogy to the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ of the mutual diffusion coefficient (Equation 11), we define the relative deviation $\Delta D_{i,\mathrm{self,rel}}$ between the real self-diffusion coefficient $D_{i,\mathrm{self}}$ and the predicted self-diffusion coefficient $D_{i,\mathrm{self,pred}}$ by the McCarty-Mason equation (Equation 6),

$$\Delta D_{i,\mathrm{self,rel}} = \frac{D_{i,\mathrm{self}} - D_{i,\mathrm{self,pred}}}{D_{i,\mathrm{self}}}, \tag{14}$$

which is a measure for non-ideal effects of self-diffusion. If the relative deviation $\Delta D_{i,\mathrm{self,rel}}$ can be described as a function $f(\Gamma)$ of the thermodynamic factor, predictions of the McCarty-Mason equation (Equation 6) can be corrected to obtain a predictive equation for non-ideal mixtures:

$$\Delta D_{i,\mathrm{self,rel}} = \frac{D_{i,\mathrm{self}} - D_{i,\mathrm{self,pred}}}{D_{i,\mathrm{self}}} = f(\Gamma), \tag{15}$$

$$\frac{1}{D_{i,\mathrm{self}}} = \frac{1}{D_{i,\mathrm{self,pred}}} \cdot (1 - f(\Gamma)) \tag{16}$$

$$= \left(\frac{x_1}{D_{i,\mathrm{self}}^{x_1 \to 1}} + \frac{x_2}{D_{i,\mathrm{self}}^{x_2 \to 1}} \right) \cdot (1 - f(\Gamma)) \,. \tag{17}$$

In this work, we investigate correlations between both the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ of mutual diffusion coefficients and the relative deviation $\Delta D_{i,\mathrm{self,rel}}$ of self-diffusion coefficients with the thermodynamic factor Γ. We expect the thermodynamic factor to cover all nonidealities such that there is no need for further correction factors such as viscosity. To have a full and consistent set of transport data and thermodynamic data, we use MD simulations of LJ systems for our analysis. The correlations are then tested with experimental data of molecular systems.

3 Simulation Details

Our analysis is based on MD simulations of LJ systems. In the following, we provide a short overview of the specifications of the simulations. For more details and numeric results, the reader is referred to Jamali et al.[52]

We performed 250 distinct MD simulations of binary LJ systems. All parameters and properties of these simulations are reported in reduced units. The parameters of the first species serve as base units: diameter $\sigma_1 = \sigma = 1$, interaction energy $\epsilon_1 = \epsilon = 1$, and mass $m_1 = m = 1$. The parameters of the second species and the adjustable parameter k_{ij} of the Lorentz-Berthelot mixing rule are listed in Table 1. To cover a broad range of nonidealities, the ratios of the parameters of the first and second species are varied over a large range. The reduced temperature T and pressure p are $T = 0.65$ and $p = 0.05$. For each specified LJ system, two different types of simulations were performed: simulations to determine transport properties and simulations to determine thermodynamic factors.

Transport properties were calculated from equilibrium MD simulations with 200 million time steps with a time step length of 0.001 in reduced units. The transport coefficients were calculated from time-correlation functions. The Einstein relations were used to sample the time-correlations, i.e. the displacements of particles were sampled over time.[65,66] The

Table 1: Specifications of the studied LJ systems. LJ particle of type 1 has $\sigma_1 = \sigma = 1.0$, $\epsilon_1 = \epsilon = 1.0$, and mass $= m_1 = 1.0$ in reduced units .[65] k_{ij} is an adjustable parameter to the Lorentz-Berthelot mixing rule $\epsilon_{ij} = \sqrt{\epsilon_1 \epsilon_2}\,(1 - k_{ij})$, controlling the nonideality of the systems.

Specification	Values
Total number of particles	500, 1000, 2000, 4000
Independent simulations	10, 10, 5, 5
x_1	0.1, 0.3, 0.5, 0.7, 0.9
ϵ_2/ϵ_1	1.0, 0.8, 0.6, 0.5
σ_2/σ_1	1.0, 1.2, 1.4, 1.6
m_2/m_1	$(\sigma_2/\sigma_1)^3$
k_{ij}	0.05, 0.0, -0.3, -0.6

self-diffusion coefficients follow from[13]

$$D_{i,\text{self}} = \lim_{t\to\infty} \frac{1}{6N_i t} \left\langle \sum_{j=1}^{N_i} \left(\boldsymbol{r}_{j,i}(t) - \boldsymbol{r}_{j,i}(0) \right)^2 \right\rangle \tag{18}$$

where t is the correlation time, N_i is the number of molecules of species i and $\boldsymbol{r}_{j,i}$ is the position of j-th molecule of species i. The angle brackets denote an ensemble average. The velocity crosscorrelations CC_{ii} and CC_{ij} follow from[13]

$$CC_{ii} = \lim_{t\to\infty} \frac{1}{6Nt} \left\langle \left(\sum_{k=1}^{N_i} \left(\boldsymbol{r}_{k,i}(t) - \boldsymbol{r}_{k,i}(0) \right) \right) \cdot \left(\sum_{l=1, l\neq k}^{N_i} \left(\boldsymbol{r}_{l,i}(t) - \boldsymbol{r}_{l,i}(0) \right) \right) \right\rangle, \tag{19}$$

$$CC_{ij} = \lim_{t\to\infty} \frac{1}{6Nt} \left\langle \left(\sum_{k=1}^{N_i} \left(\boldsymbol{r}_{k,i}(t) - \boldsymbol{r}_{k,i}(0) \right) \right) \cdot \left(\sum_{l=1}^{N_j} \left(\boldsymbol{r}_{l,j}(t) - \boldsymbol{r}_{l,j}(0) \right) \right) \right\rangle \tag{20}$$

where N is the total number of particles in the mixture.

The values of the transport coefficients depend on the box size of the MD simulations. More precisely, the transport coefficients scale linearly with the inverse of the box size, $1/L$. To correct for these finite-size effects, each LJ system was simulated for four different system sizes (500, 1000, 2000, and 4000 particles). Subsequently, the transport coefficients were extrapolated linearly to an infinite box size, i.e. $1/L \to 0$, to obtain the transport coefficients in the thermodynamic limit.

For the calculation of thermodynamic factors, equilibrium MD simulations with large systems consisting of 25000 particles were performed. The thermodynamic factors were calculated from Kirkwood-Buff coefficients (cf. Equation 9). The Kirkwood-Buff coefficients were calculated from integrals of the radial distribution functions (RDFs). Both the RDFs and the Kirkwood-Buff integrals were corrected for finite-size effects using the method of Ganguly and van der Vegt[67] and Milzetti et al.[50] for the RDFs and the method of Krüger et al.,[48] Dawass et al.[68] and Krüger and Vlugt[69] for the Kirkwood-Buff integrals. Each simulation for the calculation of thermodynamic factors was performed for 10 million time steps with a time step length of 0.001 in reduced units. All simulations were repeated for at least five times to assess statistical uncertainties.

4 Results and Discussion

The MD simulations provide a full set of transport data and thermodynamic properties. Thereby, the MD simulations enable a comprehensive analysis of non-ideal effects of mutual and self-diffusion coefficients. In Section 4.1, we analyze the correlation between the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ of mutual diffusion coefficients and the thermodynamic factor Γ. We assess the performance of the Moggridge equation (Equation 3) and confirm its validity for a wide range of non-ideal mixtures. In Section 4.2, we investigate the correlation between the relative deviation $\Delta D_{i,\mathrm{self,rel}}$ of self-diffusion coefficients with the thermodynamic factor Γ. We derive an improved model for the prediction of concentration-dependent self-diffusion coefficients in non-ideal binary mixtures (Section 4.2.1) and validate our model with experimental data (Section 4.2.2).

4.1 Mutual diffusion coefficients

The nonideality of mutual MS diffusion coefficients $Đ_{12}$ is represented by the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ (Equation 11). According to Equation 13, we can assume a correlation

between the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ and the thermodynamic factor Γ. Figure 1 shows the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ as a function of the thermodynamic factor Γ. The data of our MD simulations are a continuous function of the thermodynamic factor Γ. For the considered LJ systems, the thermodynamic factor is in the range $0.28 < \Gamma < 9$ and the relative nonidealities are in the range $-0.34 < Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}} < 0.47$, i.e. the MS diffusion coefficient $Đ_{12}$ differs from the ideal Darken diffusion coefficient by up to 47 %. For ideal mixtures without molecular interactions ($\Gamma = 1$), the velocity crosscorrelations vanish and thereby the relative nonideality vanishes: $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}} = 0$. For self-associating mixtures ($\Gamma < 1$), the velocity crosscorrelations CC_{ii} between particles of the same component i become predominant and the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ is positive. For mixtures with associating behavior between unlike particles of different components i and j, the velocity croscorrelations CC_{ij} become predominant and the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ is negative.

To validate our MD simulation data, we compare it to experimental data from literature. Table 2 provides a detailed list of references for the experimental data used in this work. The experimental datasets consist of mutual Fick diffusion coefficients D_{12}, self-diffusion coefficients $D_{i,\mathrm{self}}$, and thermodynamic factors Γ. The self-diffusion coefficients $D_{i,\mathrm{self}}$ originate from NMR measurements or diffusion measurements with radioactive tracers; the thermodynamic factors Γ are either reported directly in literature or calculated from Redlich-Kister (RK) and/or NRTL parameters reported in literature. The relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ is calculated from the experimental datasets via combination of Eqs. 10 and 7:

$$Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}} = \frac{Đ_{12} - Đ_{\mathrm{Darken}}}{Đ_{\mathrm{Darken}}} \tag{21}$$

$$= \frac{D_{12}/\Gamma}{Đ_{\mathrm{Darken}}} - 1 \tag{22}$$

$$= \frac{D_{12}/\Gamma}{x_2 D_{1,\mathrm{self}} + x_1 D_{2,\mathrm{self}}} - 1. \tag{23}$$

The thermodynamic factors of the experimental data are in the range $0 < \Gamma < 2$. Figure 1 provides an inset for the range $0 < \Gamma < 2$. Overall, our MD data agree well with the experimental data. Deviations can be observed only for mixtures with dimerising species, i.e. ethanol and methanol for the current dataset. For dimerising species, the relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ is larger in comparison to non-dimerising species. This special behavior of dimerising species was also observed by Moggridge[31] and is also observed for self-diffusion coefficients below (cf. Section 4.2.2).

Figure 1 also shows the predictions of the Moggridge equation (cf. Equation 3 and Equation 13). In the typical range of thermodynamic factors of molecular systems, $0 < \Gamma < 2$, the Moggridge equation performs well and agrees with our MD data as well as with most of the experimental data. Again, mixtures with dimerising species show larger deviations from the Moggridge equation. For large thermodynamic factors $\Gamma > 2$, our MD data suggests a different functional relation than the Moggridge equation with less negative relative nonidealities $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$. However, for practical applications with typical thermodynamic factors $0 < \Gamma < 2$, the performance of the Moggridge equation is excellent.

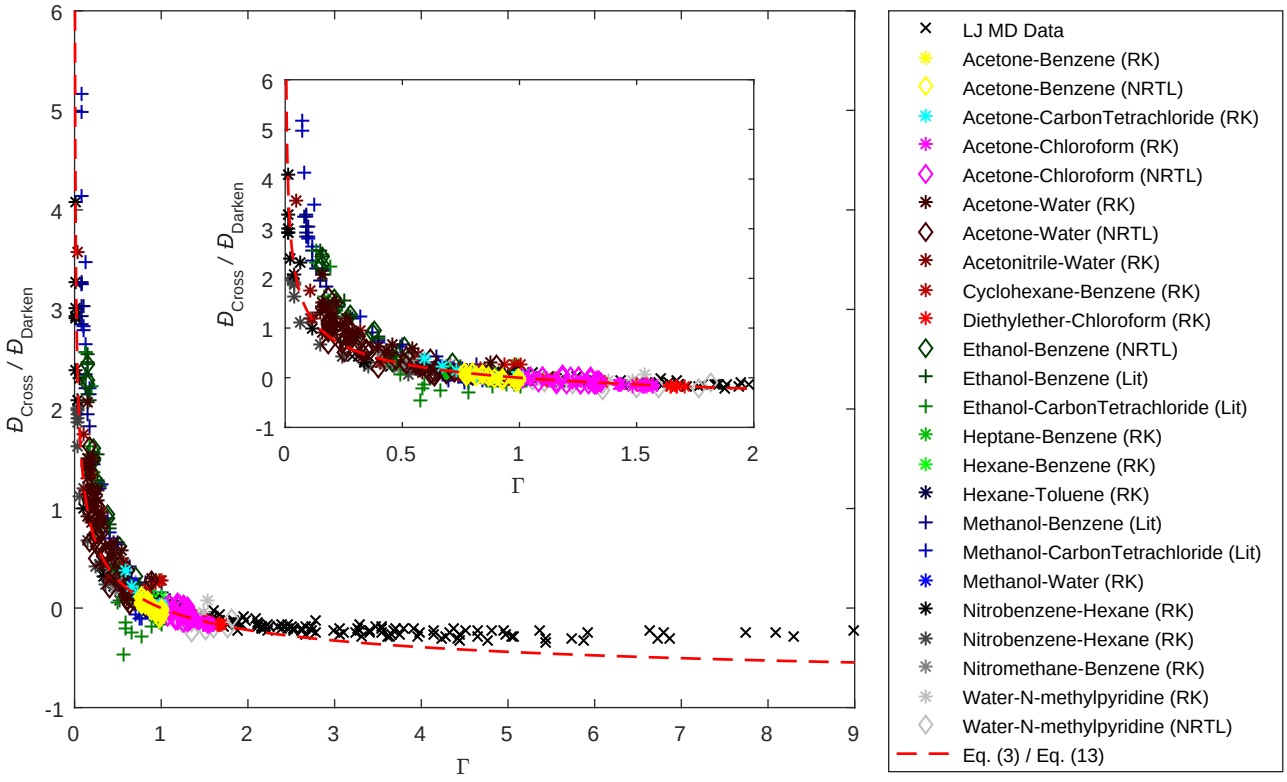

Figure 1: Relative nonideality $Đ_{\mathrm{Cross}}/Đ_{\mathrm{Darken}}$ of mutual diffusion coefficients as function of the thermodynamic factor Γ. Inset for thermodynamic factors $0 < \Gamma < 2$. Black crosses: Data from MD simulations. Stars: Experimental data with thermodynamic factors calculated with Redlich-Kister (RK). Diamonds: Experimental data with thermodynamic factors calculated with NRTL. Plus symbols: Experimental data with thermodynamic factors given in literature. Red dashed line: Predictive Moggridge equation (Equation 3). Statistical uncertainties of the MD data are given in Jamali et al.[52] References for the experimental data are provided in Table 2.

Table 2: References for the experimental data used in this work.

System	Diffusion coefficients			Thermodynamic factor		
	D_{12}	$D_{1,\text{self}}$	$D_{2,\text{self}}$	Redlich-Kister (RK)	NRTL	reported in Literature (Lit)
Acetone-Benzene	Anderson et al.[70], Cullinan and Toor[72]	Yoshinobu and Yasumichi[71]	Yoshinobu and Yasumichi[71]	Moggridge[25]	Zhu et al.[32]	-
Acetone-CarbonTetrachloride	Anderson et al.[70], Cullinan and Toor[72]	Hardt et al.[73]	Hardt et al.[73]	Moggridge[25]	-	-
Acetone-Chloroform	McCall and Douglass[74], Tyn and Calus[77], Anderson et al.[70]	D'Agostino et al.[75]	D'Agostino et al.[75]	D'Agostino et al.[75]	Gmehling et al.[76]	-
Acetone-Water	Anderson et al.[70], Grossmann and Winkelmann[78], Rehfeldt and Stichlmair[79], Tyn and Calus[77], Zhou et al.[80]	Mills and Hertz[59]	Mills and Hertz[59]	Moggridge[25]	Gmehling et al.[76]	-
Acetonitrile-Water	Easteal et al.[63]	Easteal et al.[63]	Easteal et al.[63]	Fitted from data of French[81]	-	-
Cyclohexane-Benzene	Harned[82]	Mills[83]	Mills[83]	Moggridge[25]	-	-
Diethylether-Chloroform	Sanni et al.[84], Weingärtner[54]	Weingärtner[54]	Weingärtner[54]	Moggridge[25]	-	-
Ethanol-Benzene	Anderson et al.[70], Zhu et al.[32]	Johnson and Babb[85]	Johnson and Babb[85]	-	Zhu et al.[32]	Guevara-Carrion et al.[15]*
Ethanol-Carbon Tetrachloride	Hammond and Stokes[86], Longsworth[87], Bosse and Bart[88]	Hardt et al.[73]	Hardt et al.[73]	-	-	Guevara-Carrion et al.[15]*
Heptane-Benzene	Harris et al.[89]	Harris et al.[89]	Harris et al.[89]	Moggridge[25]	-	-
Hexane-Benzene	Harris et al.[89]	Harris et al.[89]	Harris et al.[89]	Moggridge[25]	-	-
Hexane-Toluene	Ghai and Dullien[90]	Ghai and Dullien[90]	Ghai and Dullien[90]	Moggridge[25]	-	-
Methanol-Benzene	Caldwell and Babb[91]	Aoyagi and Albright[92] Johnson and Babb[85]	Aoyagi and Albright[92] Johnson and Babb[85]	-	-	Guevara-Carrion et al.[15]*
Methanol-Carbon Tetrachloride	Anderson et al.[70], Prabhakar and Weingärtner[93], Longsworth[87]	Prabhakar and Weingärtner[93]	Prabhakar and Weingärtner[93]	-	-	Guevara-Carrion et al.[15]*
Methanol-Water	Chang et al.[94], Derlacki et al.[95] Bosse and Bart[88]	Derlacki et al.[95]	Derlacki et al.[95]	Moggridge[25]	-	-
Nitrobenzene-Hexane	Haase and Siry[96]	D'Agostino et al.[24]	D'Agostino et al.[24]	D'Agostino et al.[24]	-	-
Water-N-methylpyridine	Ambrosone et al.[97]	Ambrosone et al.[97]	Ambrosone et al.[97]	Moggridge[25]	Zhu et al.[32]	-

*MD simulation results verified with experimental data

4.2 Self-diffusion coefficients

The nonideality of self-diffusion coefficients $D_{i,\mathrm{self}}$ is represented by the relative deviation $\Delta D_{i,\mathrm{self,rel}}$ (Equation 14). For ideal mixtures, we expect relative deviations $\Delta D_{i,\mathrm{self,rel}} = 0$ from the predictions of the McCarty-Mason equation (Equation 6). For non-ideal mixtures, we assume that a modification of the McCarty-Mason equation with a function of the thermodynamic factor can account for non-ideal effects (cf. Equation 17). In Section 4.2.1, we analyze the correlation between the relative deviation $\Delta D_{i,\mathrm{self,rel}}$ and the thermodynamic factor Γ in non-ideal LJ systems and derive a modified McCarty-Mason equation for non-ideal mixtures. In Section 4.2.2, we validate the modified McCarty-Mason equation with experimental data.

4.2.1 Self-diffusion coefficients of LJ systems

Figure 2 (top figure) shows an example of a concentration-dependent self-diffusion coefficient $D_{1,\mathrm{self}}$ of a binary LJ system with pronounced nonideality. The specification of the LJ system is $\epsilon_2/\epsilon_1 = 0.6$, $\sigma_2/\sigma_1 = 1.2$, $m_2/m_1 = 1.728$, $k_{ij} = -0.6$.

In a first step, we test the performance of the McCarty-Mason equation (Equation 6). The McCarty-Mason equation requires the prior knowledge of self-diffusion coefficients $D_{i,\mathrm{self}}^{x_j \to 1}$ at infinite dilution and of the pure substances. In MD simulations, statistical uncertainties are very large for mixtures approaching infinite dilution of one of the components. Therefore, the MD simulations have been performed for mixtures with at least 10 mole-% of each species, i.e. $x_1 = [0.1, 0.3, 0.5, 0.7, 0.9]$. To obtain the values of $D_{1,\mathrm{self}}^{x_j \to 1}$, we performed a smoothing fit with a quadratic polynomial function to the self-diffusion coefficients $D_{1,\mathrm{self}}$. Figure 2 (top figure) shows the smoothing fit as well as the predictions of the McCarty-Mason equation. As expected, the McCarty-Mason prediction shows large deviations. However, the curvature of the concentration-dependence is retrieved.

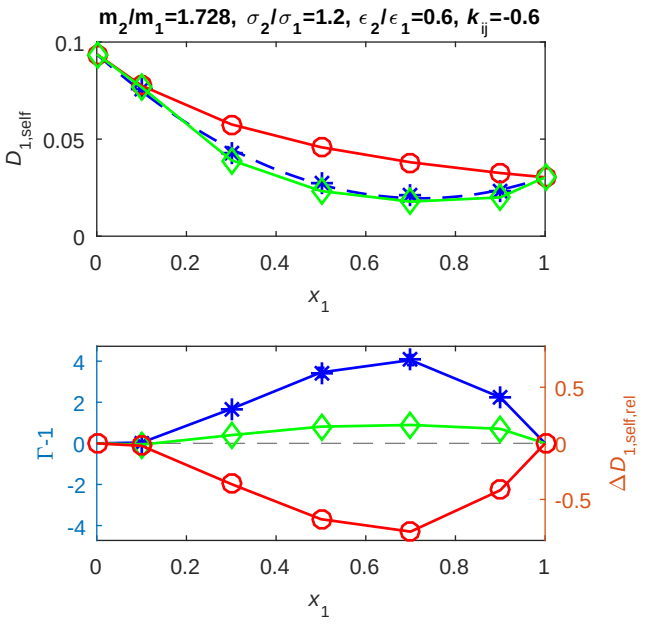

Figure 2: **Top figure**: Blue stars: Simulation results of self-diffusion coefficients $D_{1,\text{self}}$ of a binary LJ system as function of the mole fraction x_1 of the first species. Specification of the LJ system: $\epsilon_2/\epsilon_1 = 0.6$, $\sigma_2/\sigma_1 = 1.2$, $m_2/m_1 = 1.728$, $k_{ij} = -0.6$. Blue-dashed line: smoothing fit to the simulation results; red circles/line: predictions of the McCarty-Mason equation (Equation 6); green diamonds/line: predictions of the modified McCarty-Mason equation (Equation 25). The error bars of $D_{1,\text{self}}$ are smaller than the symbols.
Bottom figure: Concentration dependence of the thermodynamic factor $\Gamma - 1$ (blue stars/line, left axis) and concentration-dependence of the relative deviation $\Delta D_{i,\text{self,rel}}$ between the self-diffusion coefficients and the McCarty-Mason predictions (Equation 6) (red circles/line, right axis) and the modified McCarthy-Mason prediction (Equation 25) (green diamonds/line, right axis). A clear correlation between $\Gamma - 1$ and $\Delta D_{1,\text{self,rel}}$ can be observed. The error bars of $\Gamma - 1$ are smaller than the symbol sizes. A full set of plots for all considered LJ systems is given in the Supporting Information.

Figure 2 (bottom figure) shows the concentration dependence of the relative deviation $\Delta D_{1,\text{self,rel}}$ (Equation 14) of the predictions made by the McCarty-Mason equation. Large relative deviations up to 70 % are observed. Figure 2 (bottom figure) also shows the concentration dependence of the thermodynamic factor minus 1, $\Gamma - 1$. The term $\Gamma - 1$ is a measure for the deviation of the mixture from an ideal mixture. In the present case, $\Gamma - 1$ takes values of up to 4.2, i.e. the LJ system is highly non-ideal.

We can now compare the concentration dependencies of $\Gamma - 1$ and $\Delta D_{1,\text{self,rel}}$. Figure 2 (bottom figure) suggests a strong correlation between $\Delta D_{1,\text{self,rel}}$ and $\Gamma - 1$: Large

deviations of a mixture from ideal behavior lead to large relative deviations of the McCarty-Mason prediction.

To study the correlation between $\Delta D_{1,\mathrm{self,rel}}$ and $\Gamma - 1$ for the full set of LJ systems, we plot $\Delta D_{1,\mathrm{self,rel}}$ as function of $\Gamma - 1$ (cf. Figure 3(a)). A general trend $\Delta D_{1,\mathrm{self,rel}} \propto \Gamma - 1$ can be observed. However, the data scatters for molar mass ratios $m_2/m_1 > 2$. As a first approximation, we restrict our analysis to systems with molar mass ratios $m_2/m_1 < 2$. Figure 3(b) shows the relative deviation $\Delta D_{1,\mathrm{self,rel}}$ as function of $\Gamma - 1$ for all LJ systems with molar mass ratios $m_2/m_1 < 2$. A clear correlation $\Delta D_{1,\mathrm{self,rel}} \propto \Gamma - 1$ can be observed. For the full range of thermodynamic factors $0 < \Gamma < 7$, the McCarty-Mason predictions show large deviations of up to 130 %. The root-mean square error of $\Delta D_{i,\mathrm{self,rel}}$ is $RMSE = 35\,\%$, i.e. the McCarty-Mason predictions deviate by 35 % on average. However, molecular systems typically have thermodynamic factors in the range $0 < \Gamma < 2$ (cf. Section 4.1). Still, even in this molecular systems range ($0 < \Gamma < 2$), the McCarty-Mason predictions have an *RMSE* of 10 %.

To improve the McCarty-Mason predictions, we introduce a linear fit of $\Delta D_{i,\mathrm{self,rel}}$ as function of Γ following Equation 15. Fitting both $\Delta D_{1,\mathrm{self,rel}}$ and $\Delta D_{2,\mathrm{self,rel}}$ in the typical range of thermodynamic factors $0 < \Gamma < 2$ results in the function (cf. Figure 3(b))

$$f(\Gamma) = -0.2807 \cdot (\Gamma - 1)\,. \tag{24}$$

Insertion of Equation 24 into Equation 17 leads to an improved predictive equation for concentration-dependent self-diffusion coefficients:

$$\frac{1}{D_{i,\mathrm{self}}} = \left(\frac{x_1}{D_{i,\mathrm{self}}^{x_1 \to 1}} + \frac{x_2}{D_{i,\mathrm{self}}^{x_2 \to 1}} \right) \cdot (1 + 0.2807 \cdot (\Gamma - 1))\,. \tag{25}$$

In the rest of the manuscript, Equation 25 will be called the "modified McCarty-Mason equation". Using the modified McCarty-Mason equation, the accuracy of the predictions is doubled compared to the McCarty-Mason predictions: The *RMSE* halves from 10 % to 5 %

for $0 < \Gamma < 2$.

The improved predictions of the modified McCarty-Mason prediction are visualized for the example LJ system considered in Figure 2: Using the modified version of the McCarty-Mason prediction decreases the maximum relative deviation from $\Delta D_{1,\mathrm{self,rel}} = 70\,\%$ to $\Delta D_{1,\mathrm{self,rel}} = 12\,\%$, i.e. the predictions are improved by a factor up to $0.7/0.12 = 5.8$. A full set of plots for all considered LJ systems is provided in the Supporting Information.

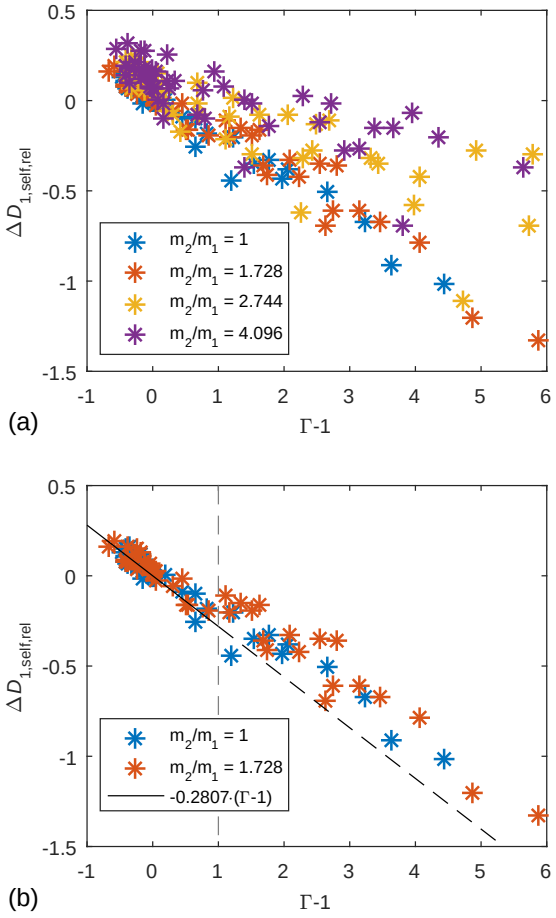

Figure 3: Relative deviations $\Delta D_{1,\mathrm{self,rel}}$ of the McCarty-Mason predictions (Equation 6) of self-diffusion coefficients as function of the thermodynamic factor Γ for LJ systems.
(a) $\Delta D_{1,\mathrm{self,rel}}$ for all LJ systems, color-coded by the molar mass ratios m_2/m_1.
(b) $\Delta D_{1,\mathrm{self,rel}}$ for LJ systems with molar mass ratios $m_2/m_1 < 2$ and best fit of Equation 15 (black line) for $0 < \Gamma < 2$ (indicated by the vertical dashed line). Plots for the second species are provided in the Supporting Information.

4.2.2 Self-diffusion coefficients of molecular systems

The modified McCarty-Mason equation (Equation 25) was obtained from MD data of LJ systems. To evaluate the practical performance of the modified McCarty-Mason equation, it has to be tested with experimental data. Figure 4(a) shows the relative deviation $\Delta D_{1,\mathrm{self,rel}}$ of the MCCarty-Mason equation (Equation 6) as function of $\Gamma - 1$. The correlation between $\Delta D_{1,\mathrm{self,rel}}$ and $\Gamma - 1$ is not as clear as for LJ systems (cf. Figure 3); even ideal mixtures ($\Gamma - 1 = 0$) have relative deviations $\Delta D_{1,\mathrm{self,rel}} \neq 0$. Still, the linear fit Equation 24, which represents the predictions of the modified McCarty-Mason equation, captures a major part of the experimental data, but some molecular systems show large deviations. In particular, the systems water-N-methypyridine and methanol-carbon tetrachloride show large deviations with completely different dependencies of $\Delta D_{1,\mathrm{self,rel}}$ on $\Gamma - 1$. This plot suggests that it may be even impossible to derive a model based on the thermodynamic factor Γ only that can capture all molecular systems.

However, the modified McCarty-Mason equation was derived for systems with molar mass ratios $M_2/M_1 < 2$. In addition, it was shown in Section 4.1 that mixtures with dimerising species need a separate analysis. Excluding systems with $m_2/m_1 < 2$ and systems with dimerising species results in the remaining dataset shown in Figure 4(b). For the remaining dataset, a clear correlation between $\Delta D_{1,\mathrm{self,rel}}$ and $\Gamma - 1$ is observed, which agrees with the linear fit Equation 24 of the modified McCarty-Mason equation. The *RMSE* of the McCarty-Mason predictions is 11 %. If the modified McCarty-Mason equation is used, the *RMSE* decreases to 5 %. Hence, the deviations of the predictions made by the modified McCarty-Mason equation are $0.11/0.05 > 2$ times lower.

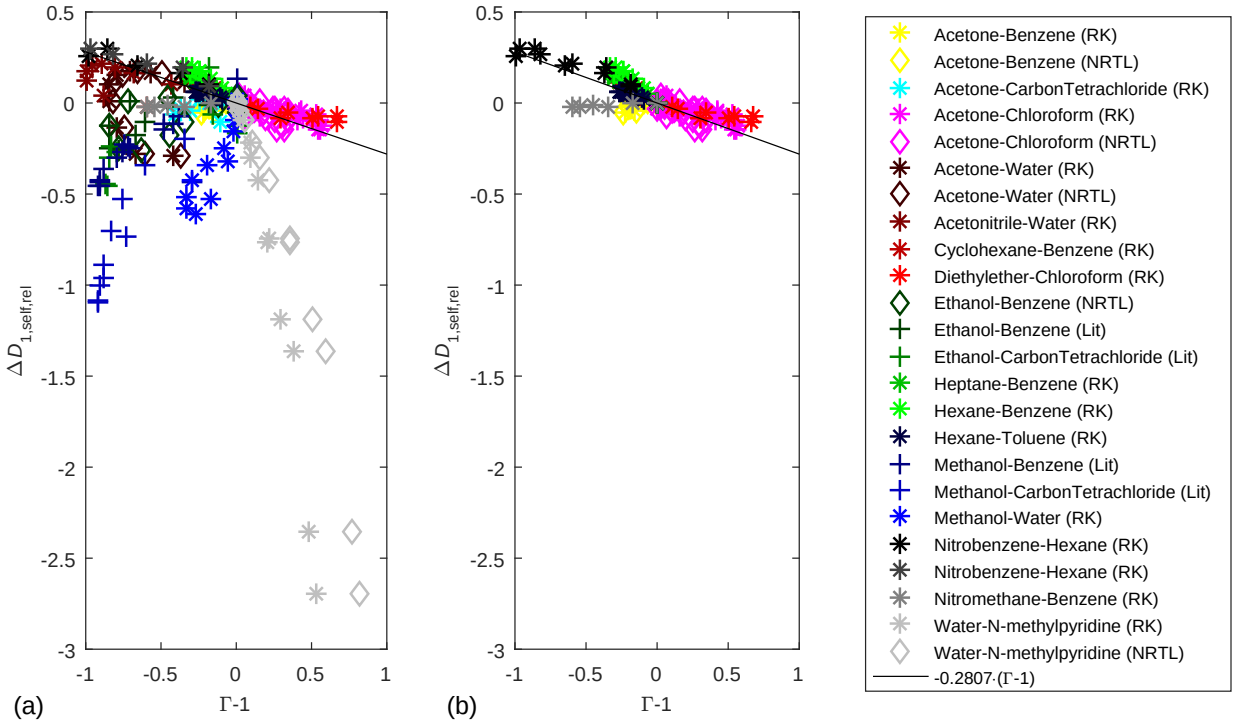

Figure 4: Relative deviations $\Delta D_{1,\mathrm{self,rel}}$ of the McCarty-Mason prediction (Equation 6) as function of the thermodynamic factor Γ for molecular systems (symbols) and linear fit of $\Delta D_{1,\mathrm{self,rel}}$ derived from LJ systems (black line, cf. Equation 24). Stars: Experimental data with thermodynamic factors calculated with Redlich-Kister (RK). Diamonds: Experimental data with thermodynamic factors calculated with NRTL. Plus symbols: Experimental data with thermodynamic factors reported in literature.
(a) $\Delta D_{1,\mathrm{self,rel}}$ for all considered molecular systems.
(b) $\Delta D_{1,\mathrm{self,rel}}$ for molecular systems with molar mass ratios $M_2/M_1 < 2$ and without dimerising species. Plots for the second species are provided in the Supporting Information.

The improvement in the prediction of self-diffusion coefficients can also be visualized in terms of the concentration dependence: Figure 5 shows experimental and predicted concentration-dependent self-diffusion coefficients of the exemplary systems nitrobenze-hexane and cyclohexane-benzene (a full set of plots for all considered molecular systems is provided in the Supporting Information). For the system nitrobenze-hexane, the *RMSE* of the McCarty-Mason prediction is 23 % and the *RMSE* of the modified McCarty-Mason prediction is 6 %. Hence, the deviation of the predictions made by the modified McCarty-Mason equation are

$0.23/0.06 \approx 4$ times lower. For the system cyclohexane-benzene, using the modified version of the McCarty-Mason equation decreases the *RMSE* from 17 % to 4 %, which also corresponds to an improvement by a factor $0.17/0.04 \approx 4$.

Hence significant improvements in the prediction of concentration-dependent self-diffusion coefficients of non-ideal binary liquid mixtures are obtained by use of the modified McCarty-Mason equation. Combining the modified McCarty-Mason equation (Equation 6) with the Moggridge equation (Equation 3) and Equation 7 leads to the following model for the prediction of concentration-dependent binary Fick diffusion coefficients:

$$D_{12} = \left(x_2 D_{1,\mathrm{self}} + x_1 D_{2,\mathrm{self}}\right) \Gamma^{0.64}, \tag{26}$$

$$\frac{1}{D_{i,\mathrm{self}}} = \left(\frac{x_1}{D_{i,\mathrm{self}}^{x_1 \to 1}} + \frac{x_2}{D_{i,\mathrm{self}}^{x_2 \to 1}} \right) \cdot \left(1 + 0.2807 \cdot (\Gamma - 1)\right), \quad i = 1, 2. \tag{27}$$

Thus, to predict concentration-dependent Fick diffusion coefficients of binary mixtures with molar mass ratios $M_2/M_1 < 2$ and without dimerising species, we need only the self-diffusion coefficients at infinite dilution $D_{i,\mathrm{self}}^{x_{j\neq i} \to 1} = D_{ij}^{x_{j\neq i} \to 1} = D_{12}^{\infty}$ and the self-diffusion coefficients of the pure substances $D_{i,\mathrm{self}}^{x_i \to 1}$ as well as the thermodynamic factor Γ of the mixture.

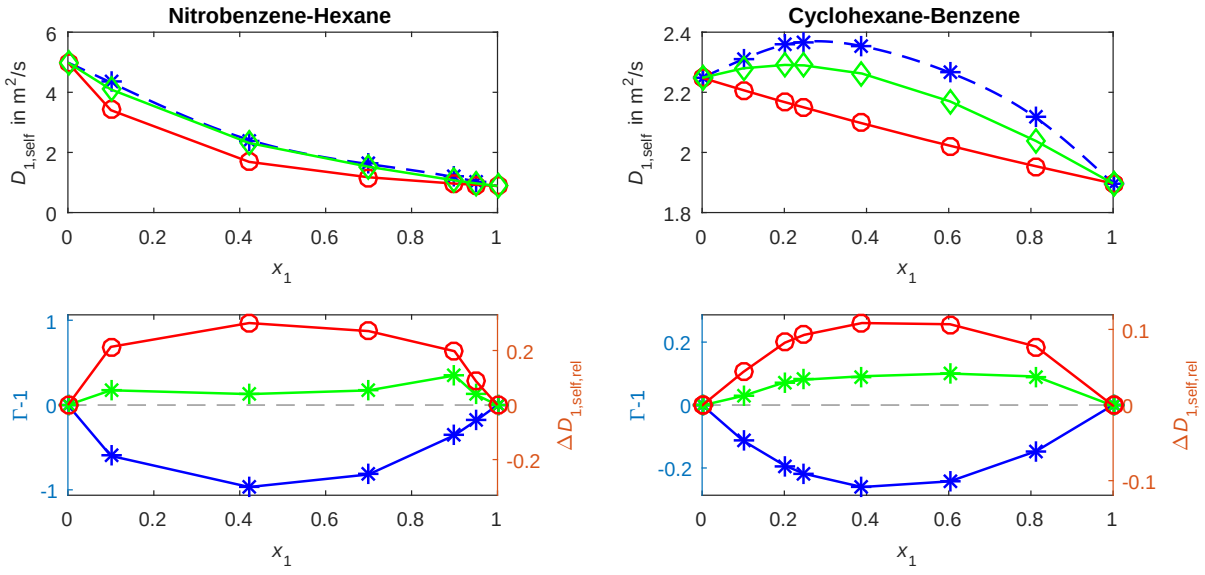

Figure 5: Concentration-dependent self-diffusion coefficients $D_{1,\mathrm{self}}$, thermodynamic factors Γ, and relative deviations $\Delta D_{i,\mathrm{self,rel}}$ for the systems nitrobenze-hexane (a) and cyclohexane-benzene (b). Note the adapted y-axis scale for each subfigure.
Top figures: Blue stars: Experimental data of concentration-dependent self-diffusion coefficients $D_{1,\mathrm{self}}$. Blue-dashed line: smoothing fit of the experimental self-diffusion coefficients; red circles/line: predictions of the McCarty-Mason equation (Equation 6); green diamonds/line: predictions of the modified McCarty-Mason equation (Equation 25).
Bottom figures: Concentration dependence of the thermodynamic factor $\Gamma - 1$ (blue stars/line, left axis) and concentration dependence of the relative deviation $\Delta D_{i,\mathrm{self,rel}}$ between the experimental self-diffusion coefficients and the McCarty-Mason predictions (Equation 6) (red circles/line, right axis) and the modified McCarthy-Mason prediction (Equation 25) (green diamonds/line, right axis).

5 Conclusions

The reliable prediction of concentration-dependent mutual diffusion coefficients has been a challenge to scientists for decades. For ideal mixtures, the physically-based Darken equation holds. For non-ideal mixtures, semi-empirical modifications of the Darken equation have been developed. However, Darken-based models rely on the knowledge of concentration-dependent self-diffusion coefficients which are rarely available.

Therefore, predictions of concentration-dependent self-diffusion coefficients are needed.

In this work, we studied the concentration-dependence of mutual and self-diffusion coefficients in non-ideal binary liquid mixtures. The basis of our analysis were data of Lennard-Jones (LJ) systems from Molecular Dynamics simulations which provide insight into the full set of transport data and thermodynamic properties. For both mutual and self-diffusion, strong correlations between non-ideal diffusion effects and the thermodynamic factor were observed. The existing modification of the Darken equation by D'Agostino et al.[24] and Moggridge[25] was confirmed to accurately predict concentration-dependent mutual diffusion coefficients for a wide range of non-ideal mixtures with typical thermodynamic factors ($0 < \Gamma < 2$). For mixtures with very large thermodynamic factors ($\Gamma > 2$), the data of the LJ systems suggest deviations.

Based on the predictive model of McCarty and Mason[44] for ideal binary gas mixtures, we developed an improved model for the prediction of concentration-dependent self-diffusion coefficients in non-ideal binary liquid mixtures. Our new model is a function of the thermodynamic factor and the self-diffusion coefficients at infinite dilution and of the pure substances which are readily available. Validation was carried out with experimental data of molecular systems. Self-diffusion coefficients of mixtures with typical thermodynamic factors $\Gamma < 2$, molar mass ratios $m_2/m_1 < 2$, and without dimerising species are successfully predicted: The relative deviation of the predictions is halved from 10 % to 5 %. In future, similar correlations may be derived for systems with dimerising species and multicomponent mixtures. Our new model thus provides the missing link to render Darken-based models into practical tools to predict mutual diffusion coefficients.

Notation

Roman Symbols

CC_{ij}	velocity crosscorrelation function between species i and j (m^2/s)

D_{12}	Fick diffusion coefficient (m^2/s)
$Đ_{12}$	Maxwell-Stefan (MS) diffusion coefficient (m^2/s)
$Đ_{\text{Darken}}$	Maxwell-Stefan diffusion coefficient in ideal mixtures computed from Darken equation (m^2/s)
$Đ_{\text{Cross}}$	non-ideal part of the Maxwell-Stefan diffusion coefficient, containing the velocity crosscorrelation functions (m^2/s)
$D_{i,\text{self}}$	concentration-dependent self-diffusion coefficient of species i (m^2/s)
$D_{i,\text{self,pred}}$	predicted concentration-dependent self-diffusion coefficient of species i (m^2/s)
$\Delta D_{i,\text{self,rel}}$	relative deviation between actual and predicted concentration-dependent self-diffusion coefficient of species i ($-$)
G_{ij}	Kirkwood-Buff coefficient between species i and j (m^3)
k_{ij}	adjustable parameter for the Lorentz- Berthelot mixing rules (Pa)
L	side length of the cubic simulation box (m)
m_i	mass of a Lennard-Jones particle of species i (m)
M_i	molar mass of species i (kg/mol)
N	total number of molecules ($-$)
N_i	number of molecules of species i ($-$)
p	hydrostatic pressure (Pa)
$\boldsymbol{r}_{l,j}$	position of molecule j of species i ($-$)
T	temperature (K)
V	volume of the simulation box (m^3)
w_i	weight fraction of species i ($-$)

x_i mole fraction of species i $(-)$

Greek Symbols

γ_i activity coefficient of species i $(-)$

Γ thermodynamic factor $(-)$

ϵ_i Lennard-Jones energy parameter for species i (ϵ)

η shear viscosity $(\mathrm{Pa} \cdot \mathrm{s})$

σ_i Lennard-Jones size parameter for species i (σ)

Superscript

$x_i \to 1$ mole fraction x_i of species i tending towards 1

∞ infinite dilution

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Supporting Information:

Prediction of concentration-dependent self-diffusion coefficients in binary liquid mixtures:

The missing link for Darken-based models

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Thijs J. H. Vlugt,[‡] and André Bardow[†]

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Contents

S1 Self-diffusion coefficients of LJ systems

S1.1 Relative deviations $\Delta D_{2,\mathrm{self,rel}}$ of the McCarty-Mason prediction as a function of the thermodynamic factor Γ for component 2

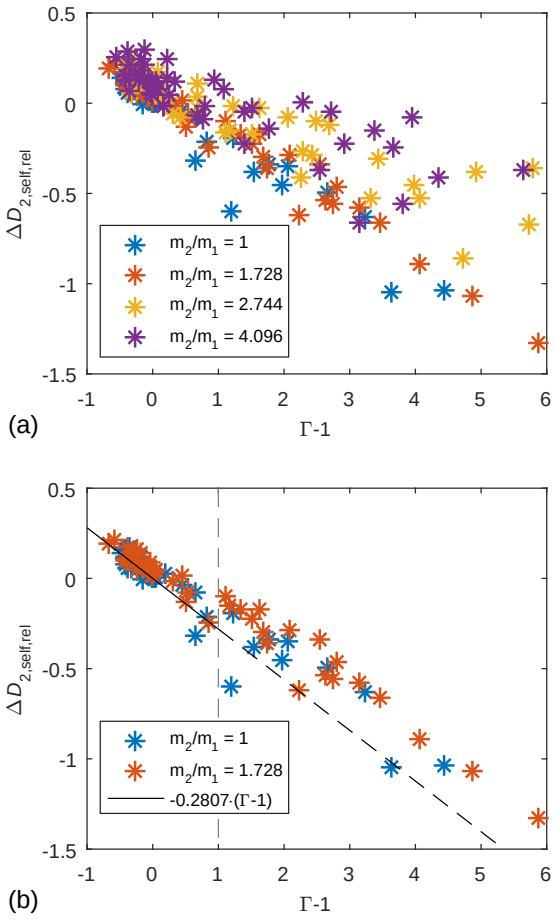
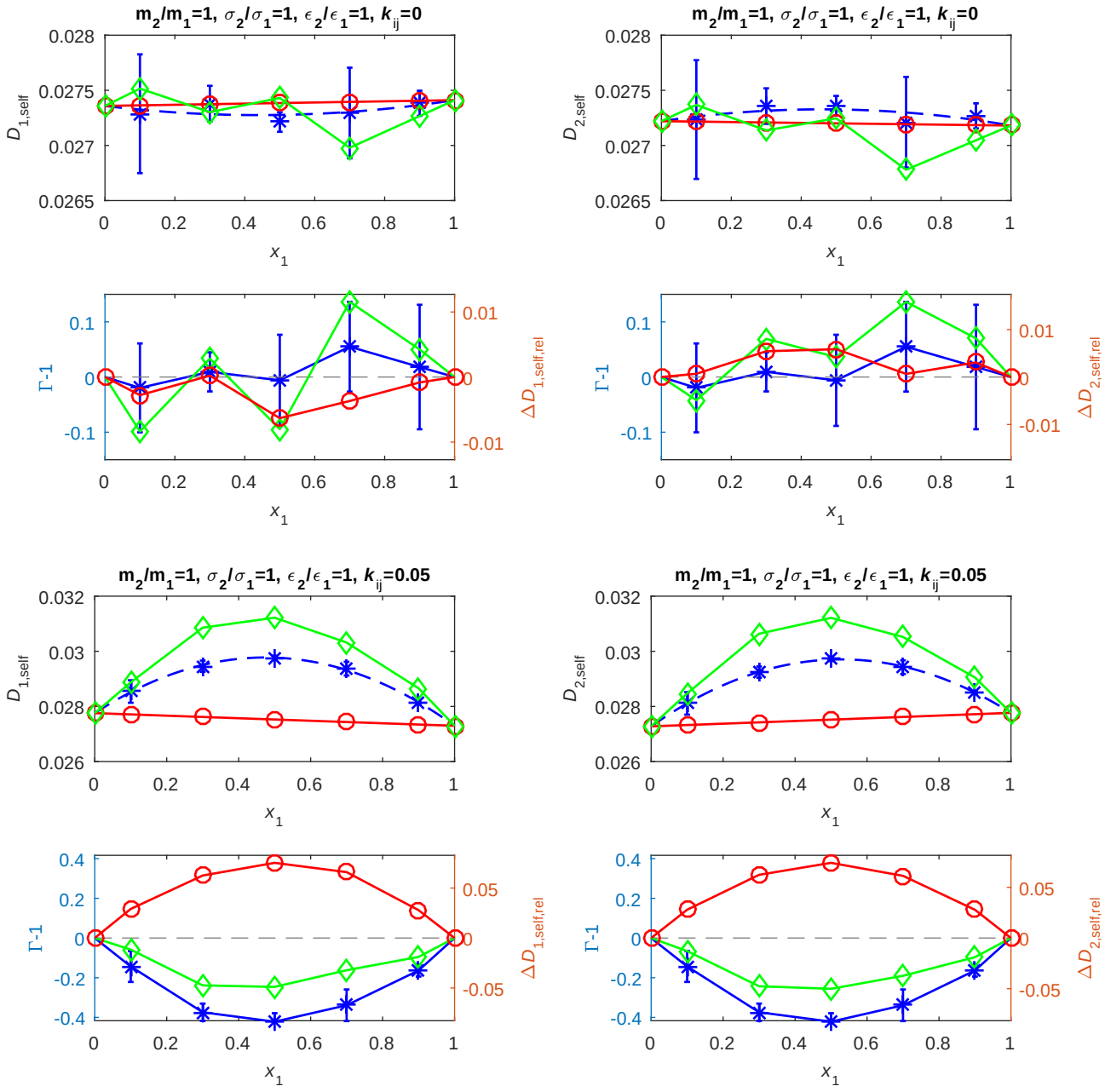
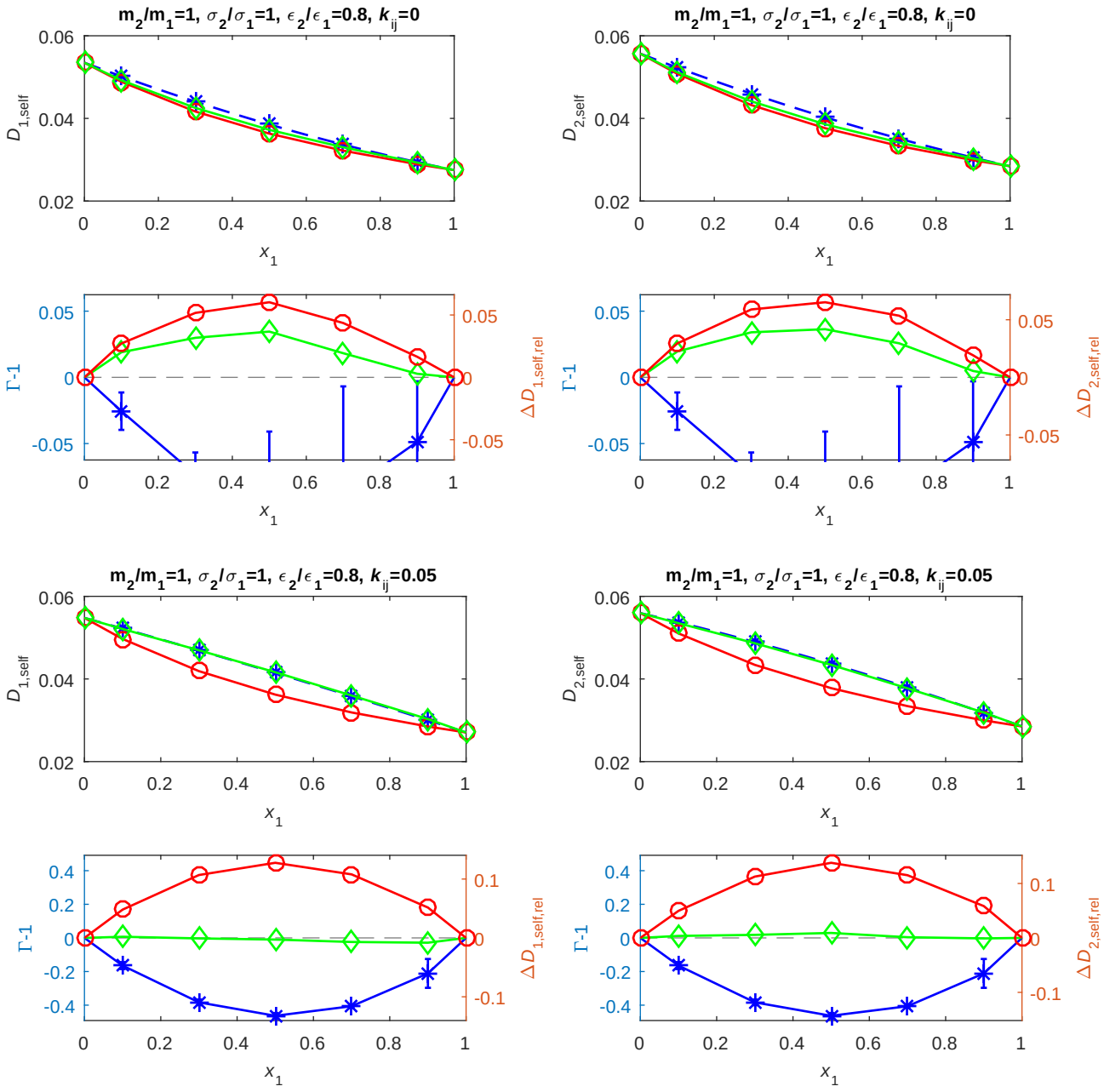


Figure S1: Relative deviations $\Delta D_{2,\mathrm{self,rel}}$ of the McCarty-Mason prediction as function of the thermodynamic factor Γ for LJ systems.
(a) $\Delta D_{2,\mathrm{self,rel}}$ for all LJ systems, differentiated by the molar mass ratios m_2/m_1.
(b) $\Delta D_{2,\mathrm{self,rel}}$ for LJ systems with molar mass ratios $m_2/m_1 < 2$ and best fit of Equation 15 (black line) for $0 < \Gamma < 2$ (indicated by the vertical dashed line).

S1.2 LJ systems with molar mass ratios $m_2/m_1 < 2$

Please note that y-axes are adapted for each system.

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Γ-1
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Γ-1
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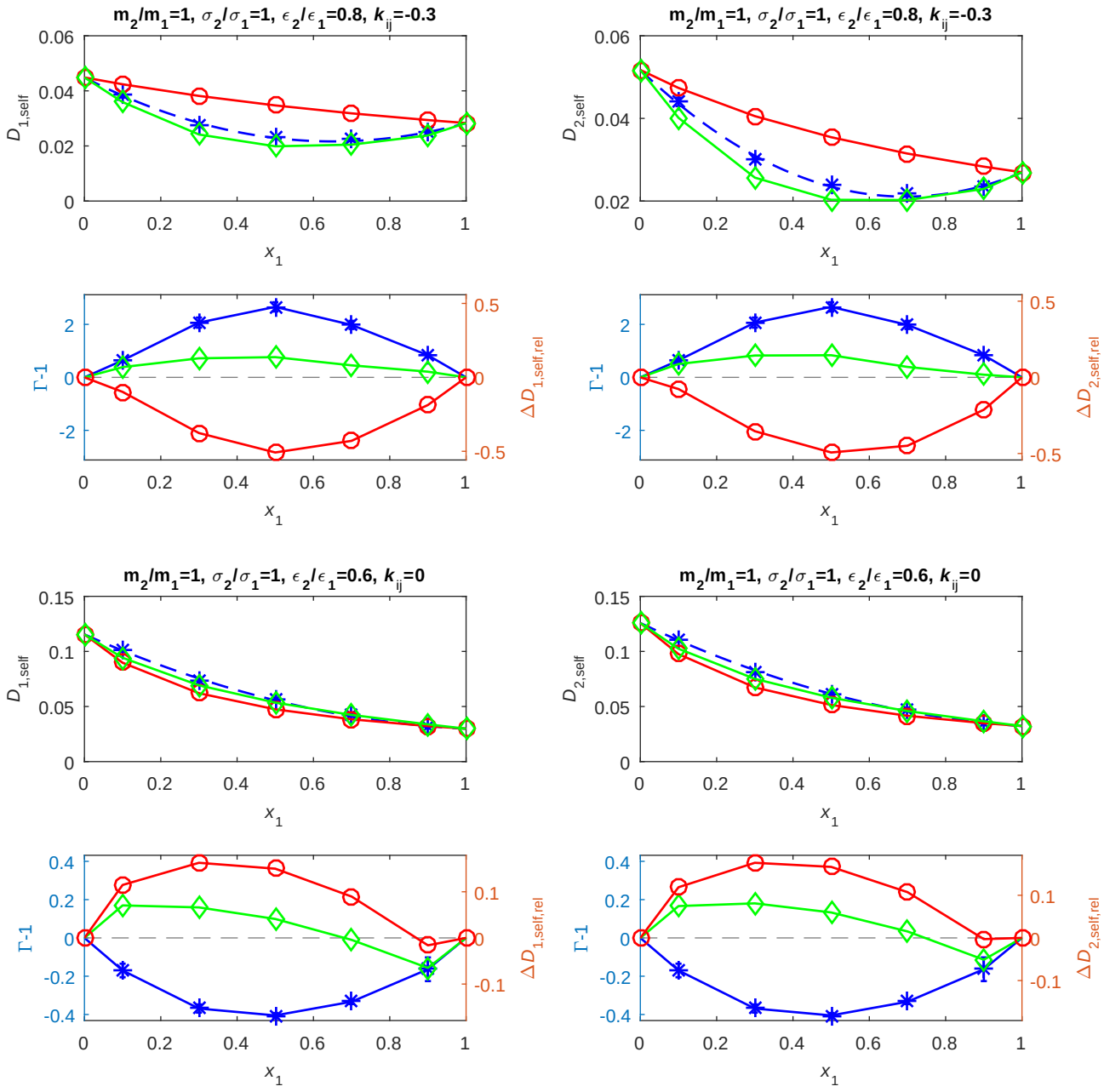
Γ-1
ΔD2,self,rel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Γ-1
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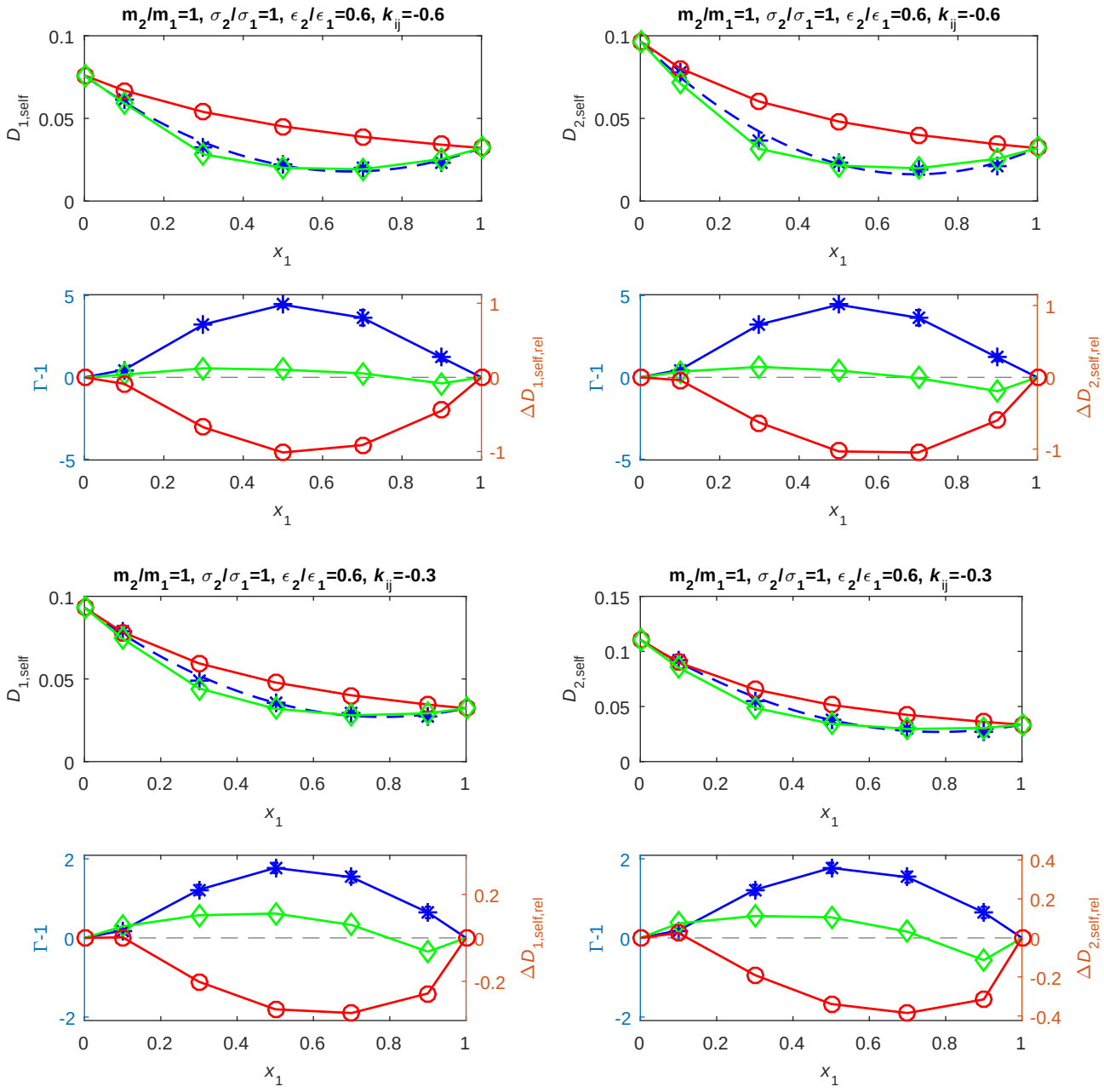
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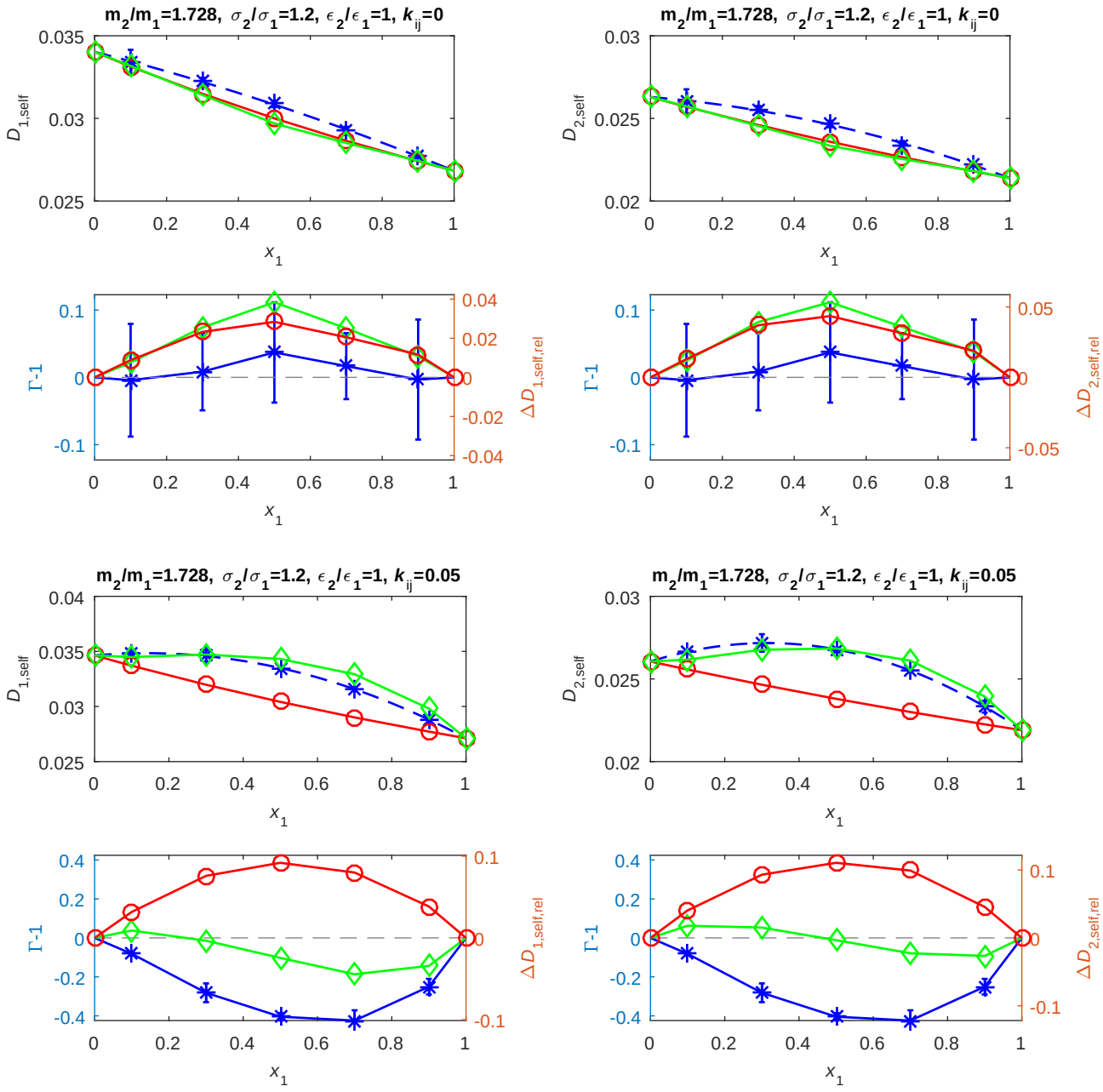
ΔD2,self,rel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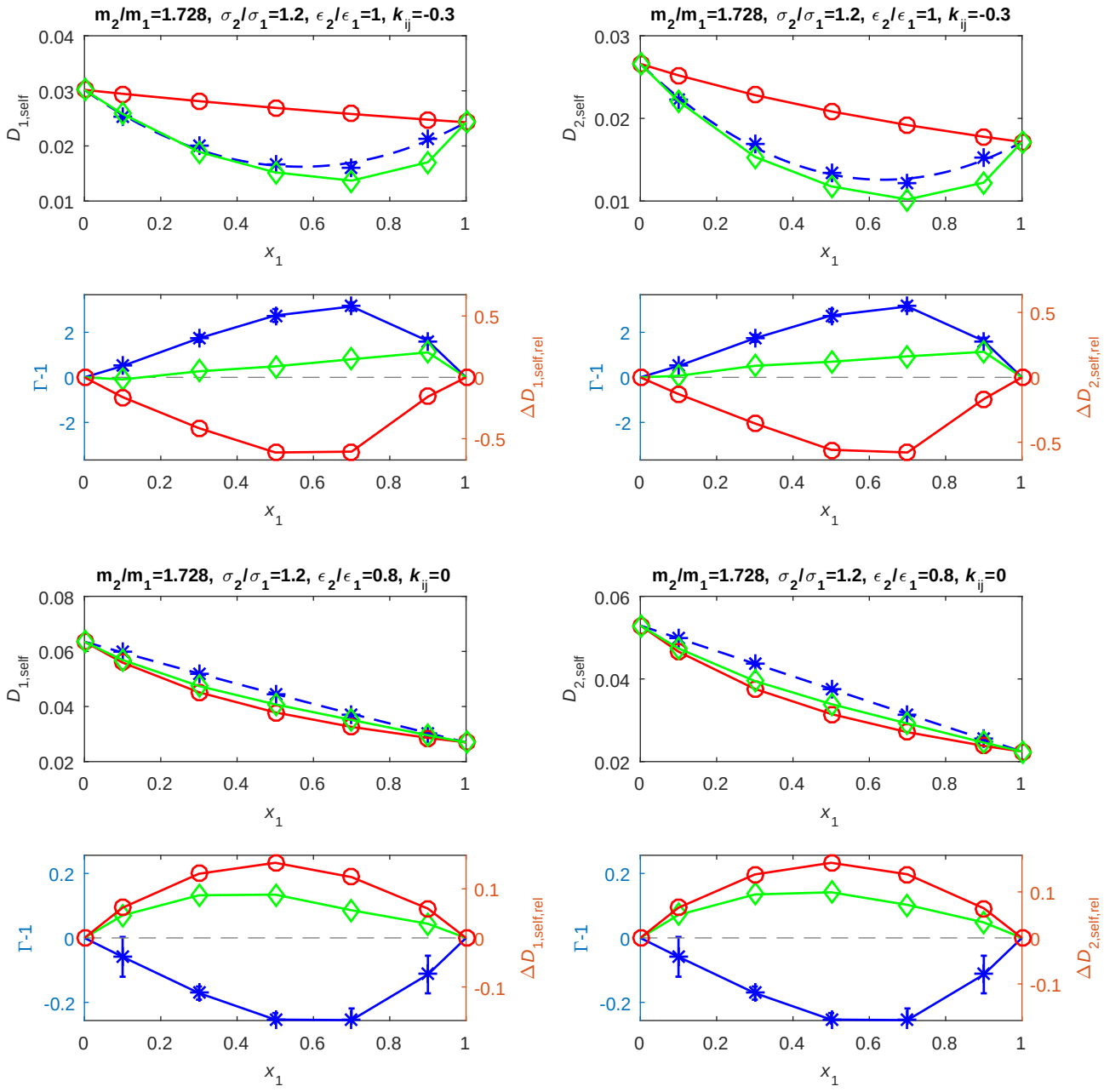
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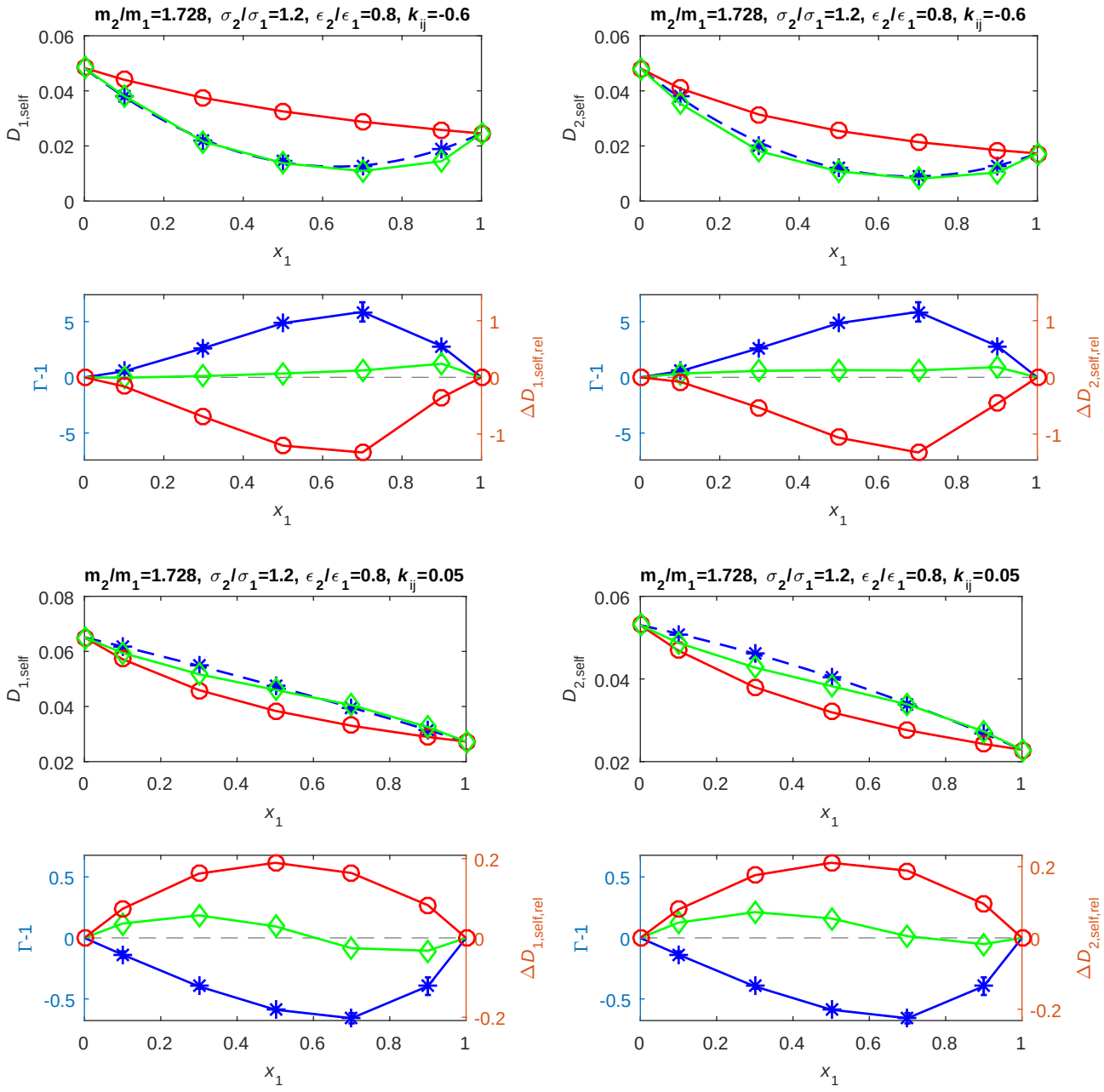
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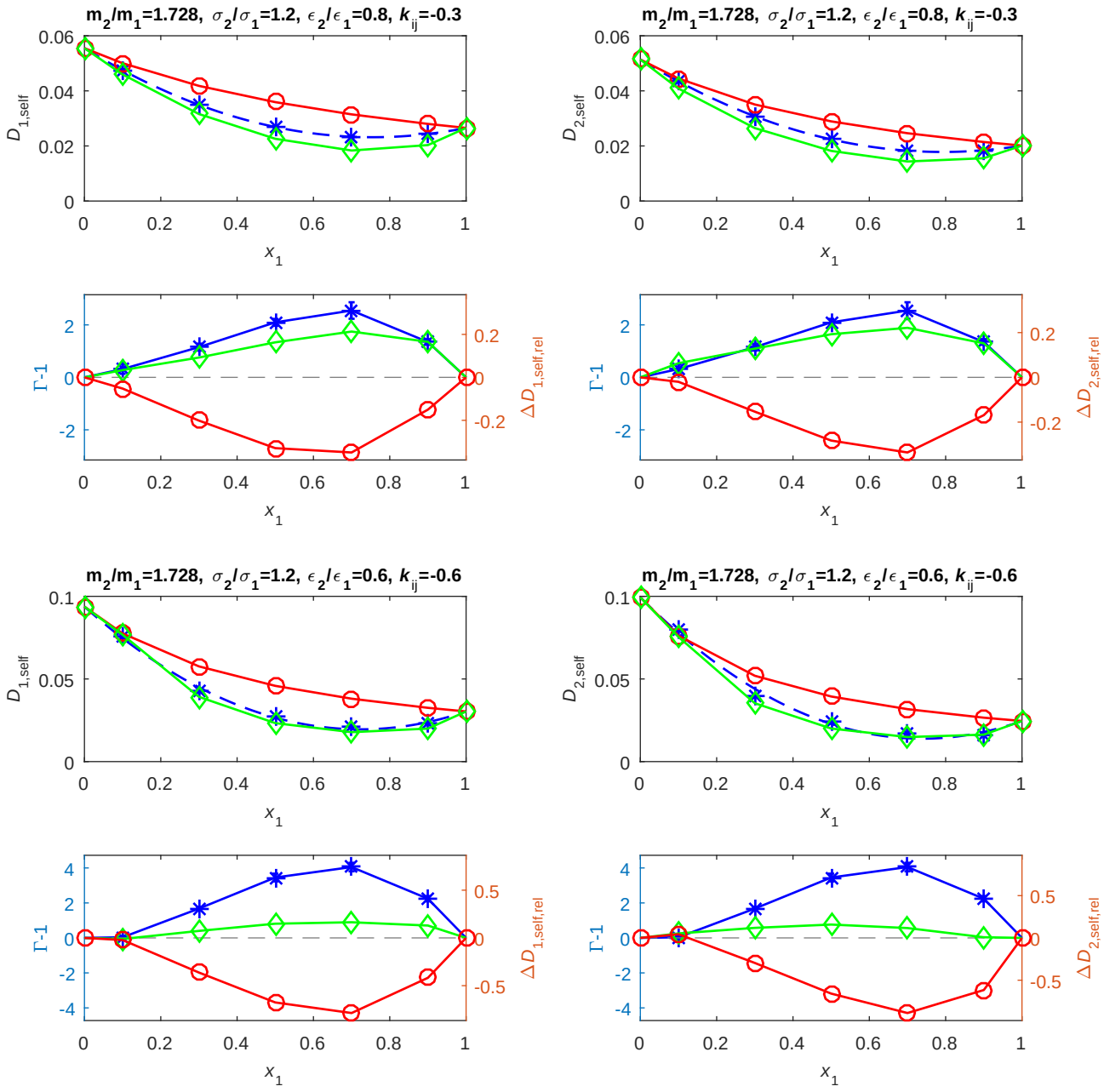
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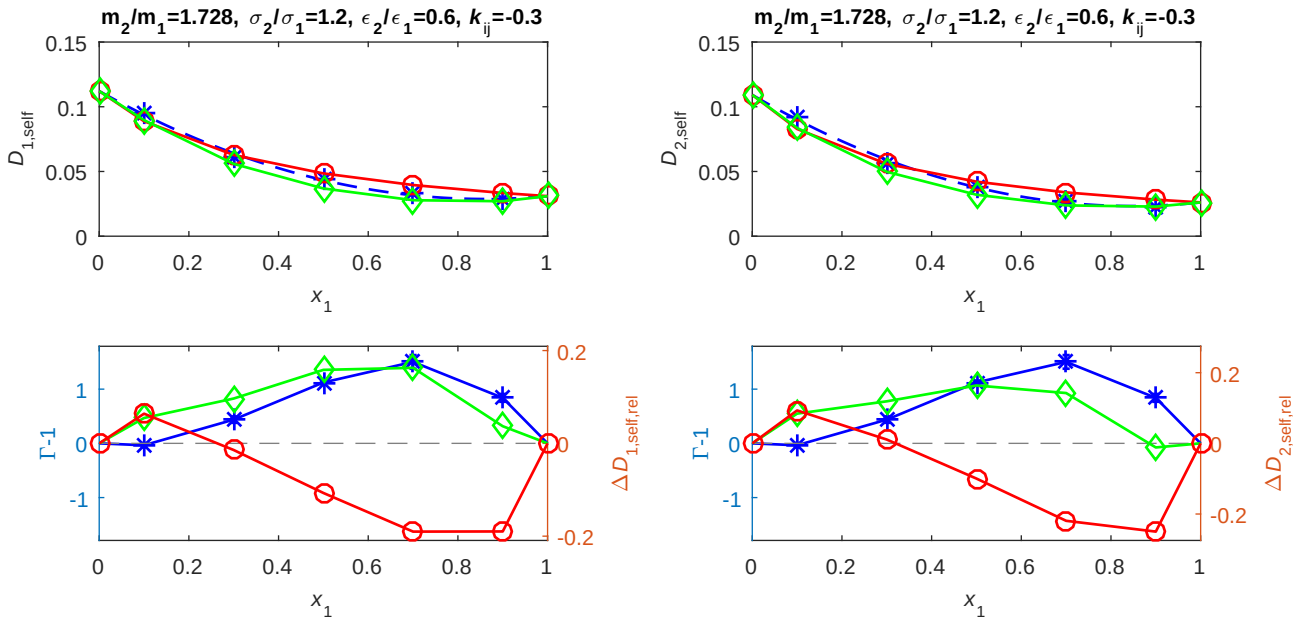
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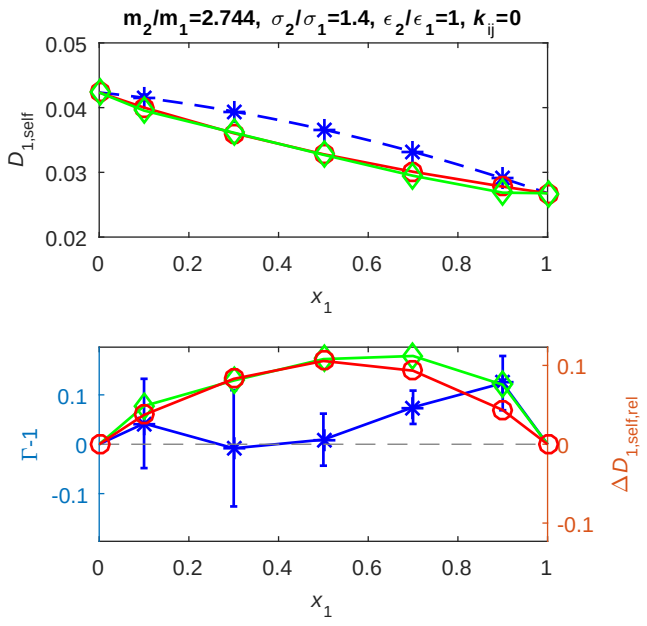
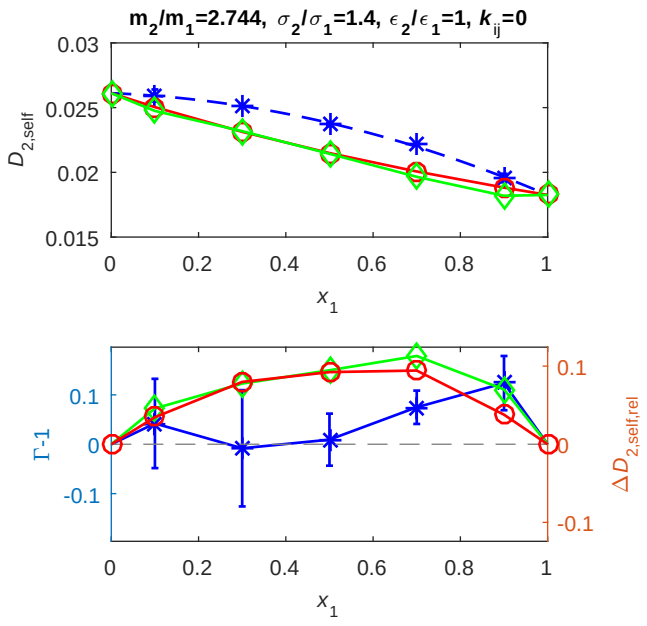
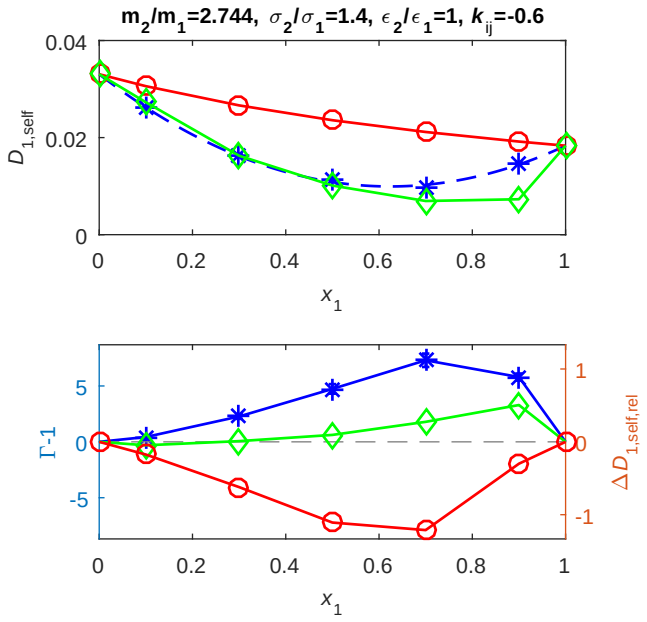
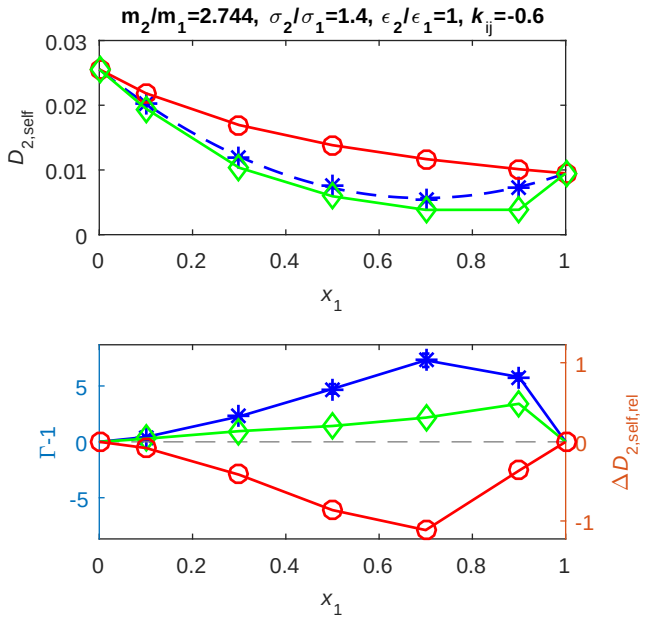
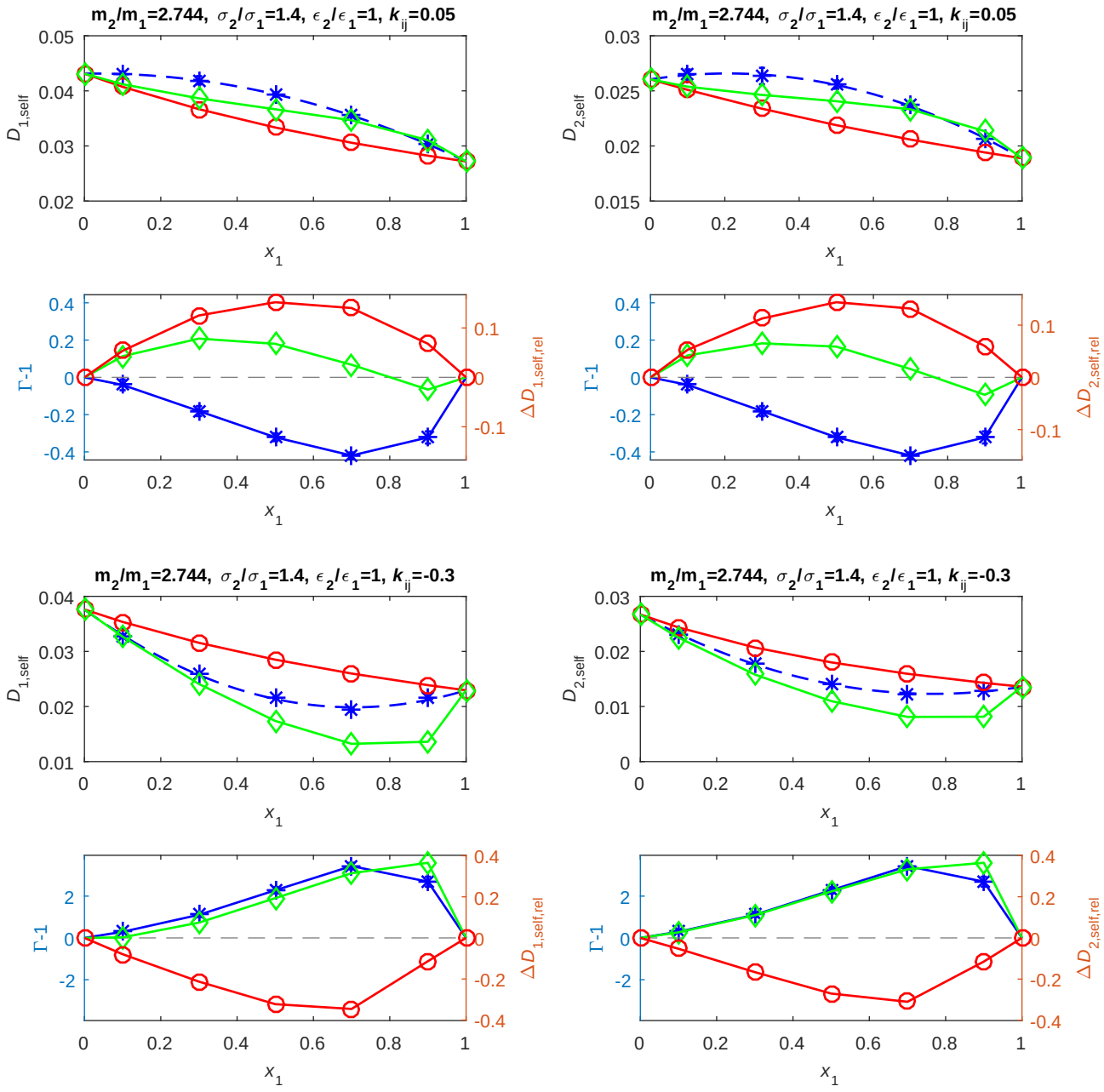
S1.3 LJ systems with molar mass ratios $m_2/m_1 > 2$







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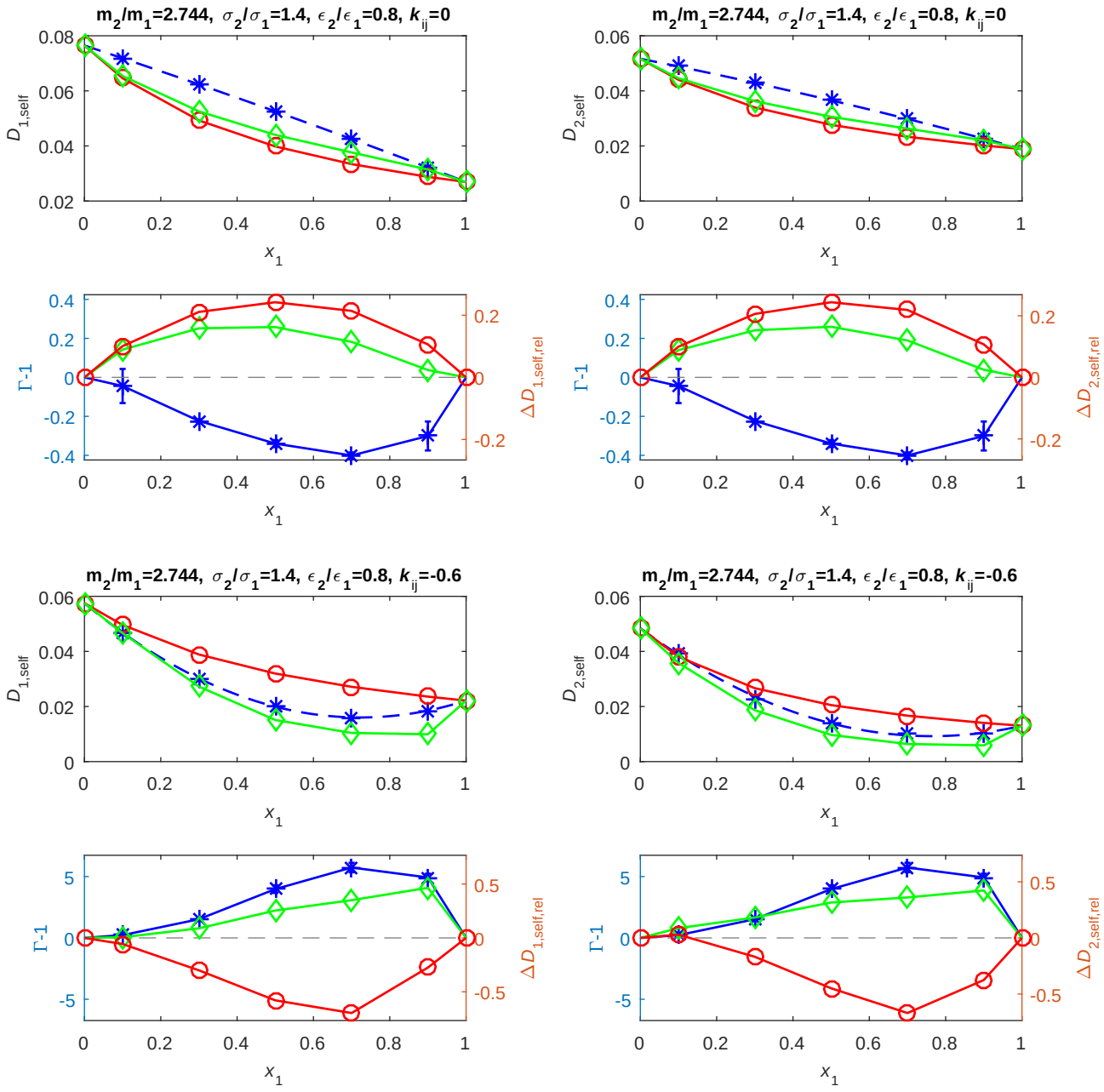
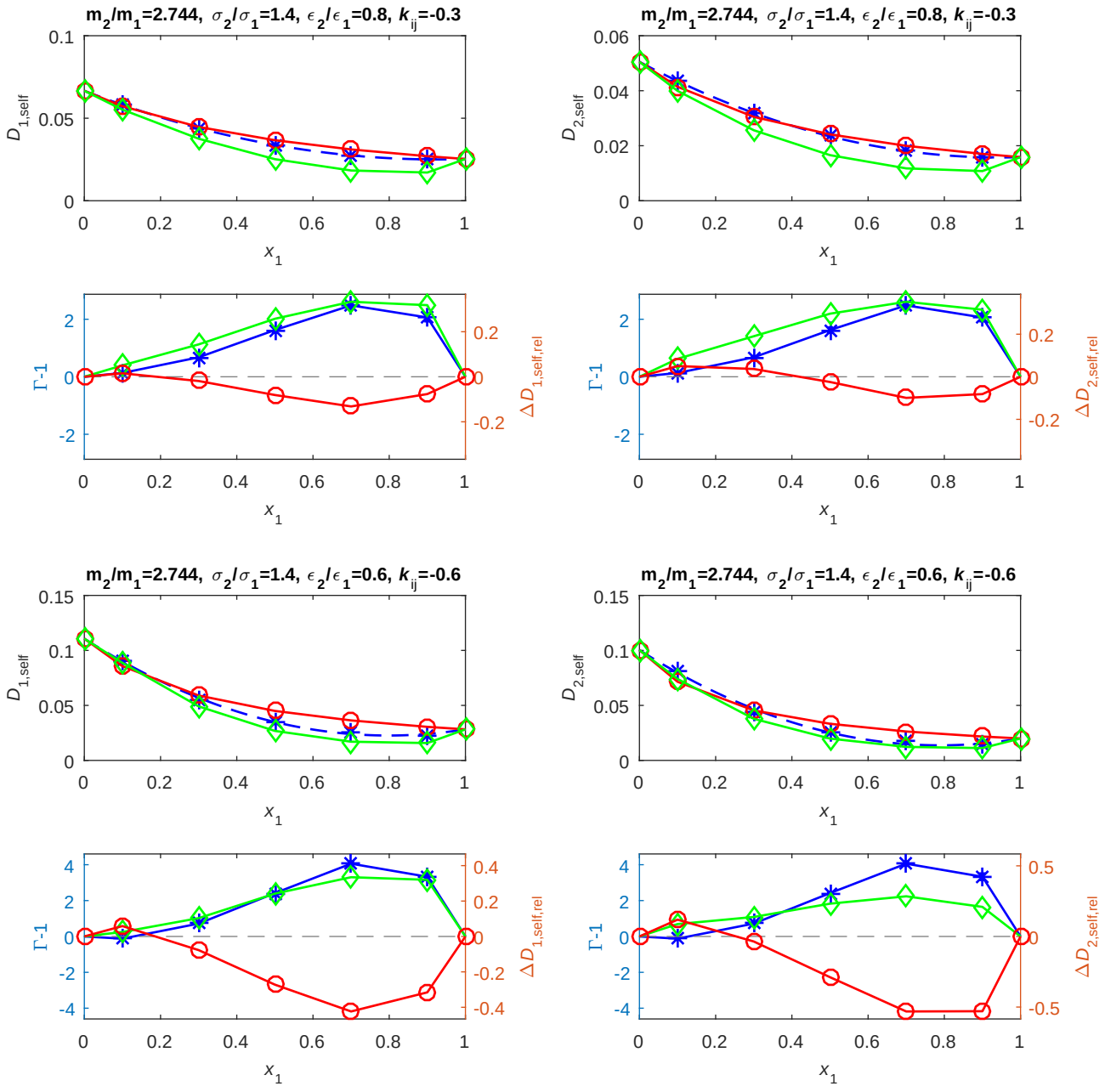
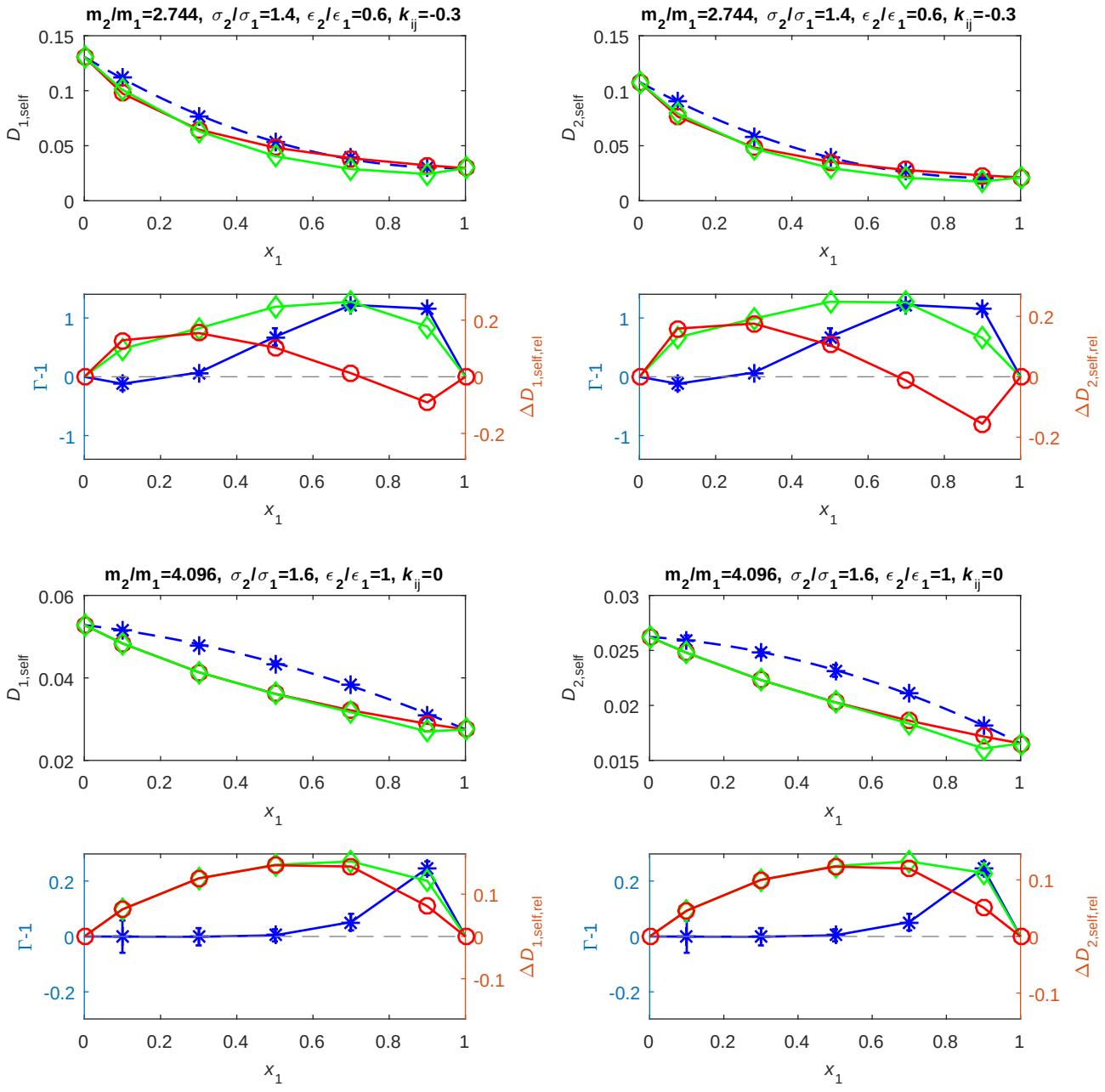
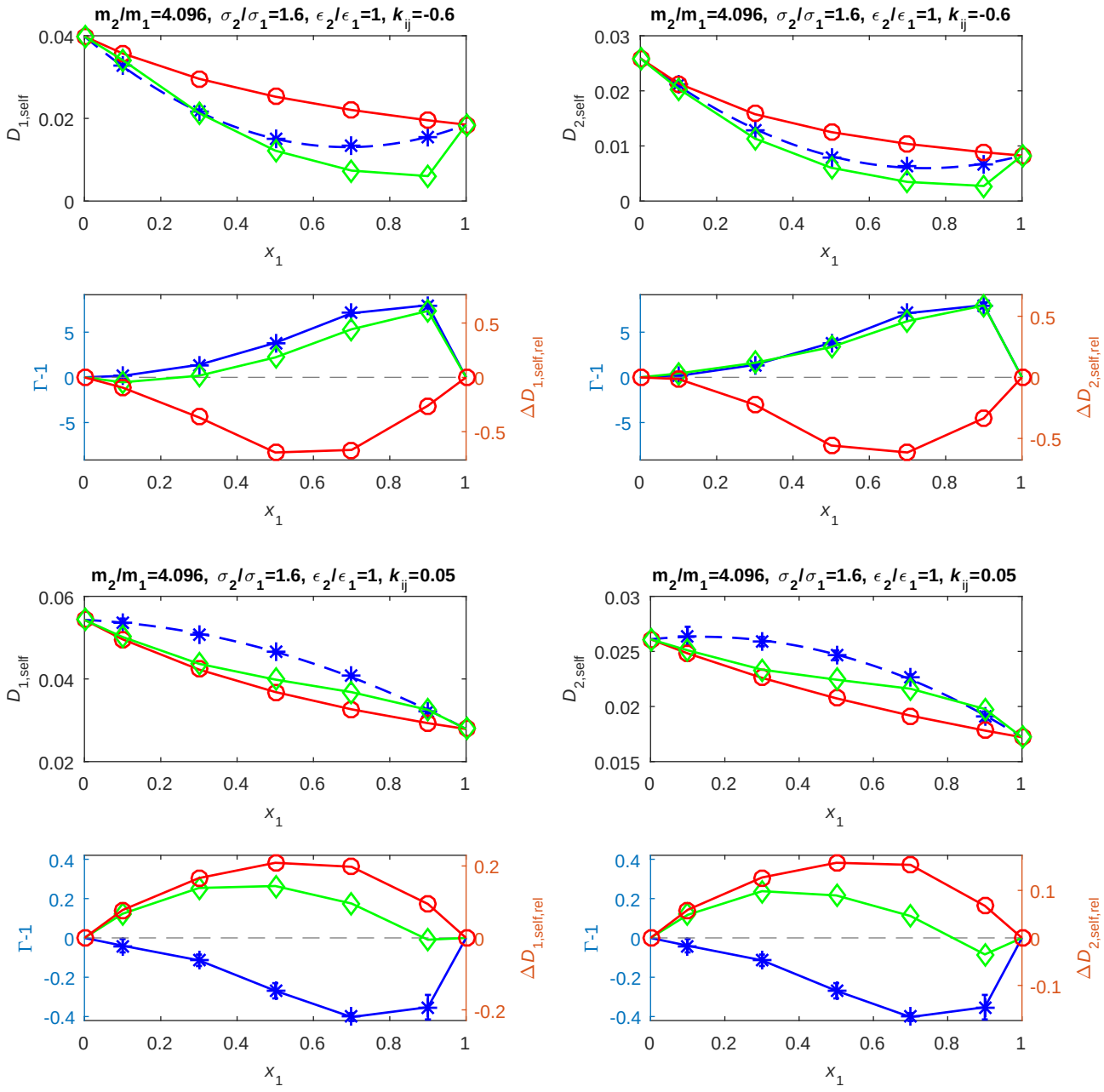
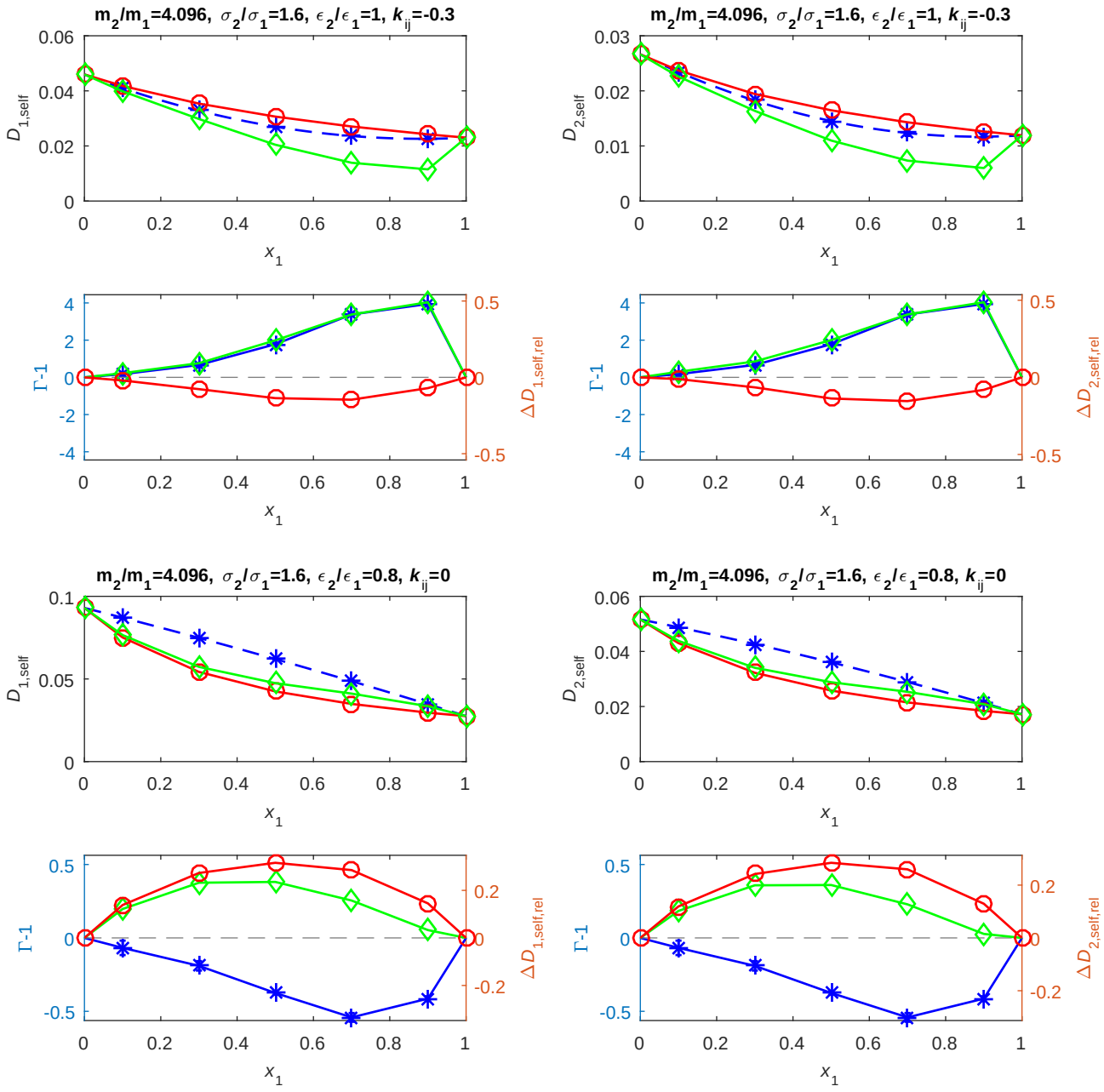
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=1, kij=-0.3
D2,self
x1
Γ-1
ΔD2,self,rel

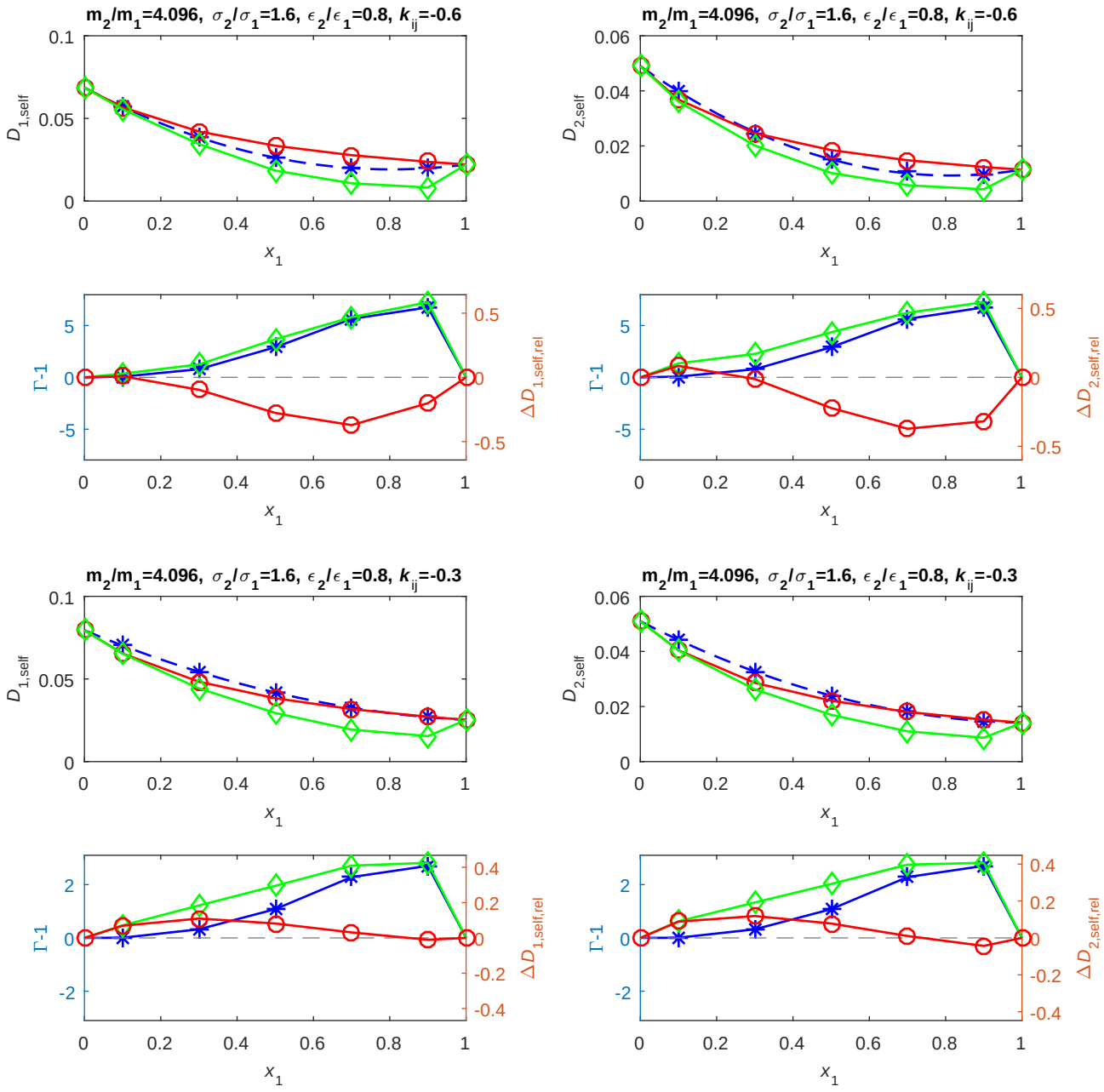

m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=0.8, kij=0
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=0.8, kij=0
D2,self
x1
Γ-1
ΔD2,self,rel
m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=0.8, kij=-0.6
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=0.8, kij=-0.6
D2,self
x1
Γ-1
ΔD2,self,rel

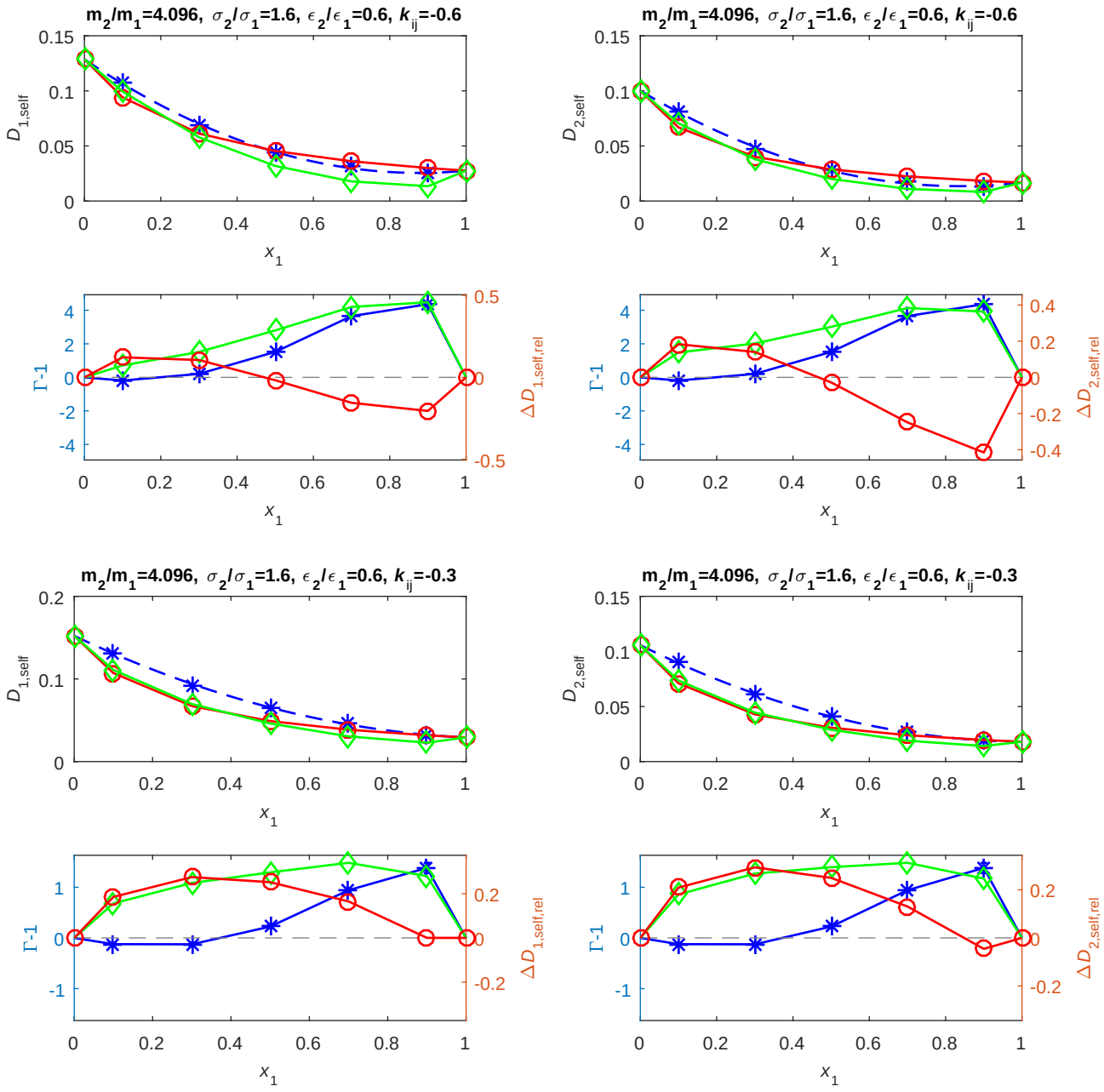

m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=0.8, kij=-0.3
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=0.8, kij=-0.3
D2,self
x1
Γ-1
ΔD2,self,rel
m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=0.6, kij=-0.6
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=2.744, σ2/σ1=1.4, ε2/ε1=0.6, kij=-0.6
D2,self
x1
Γ-1
ΔD2,self,rel

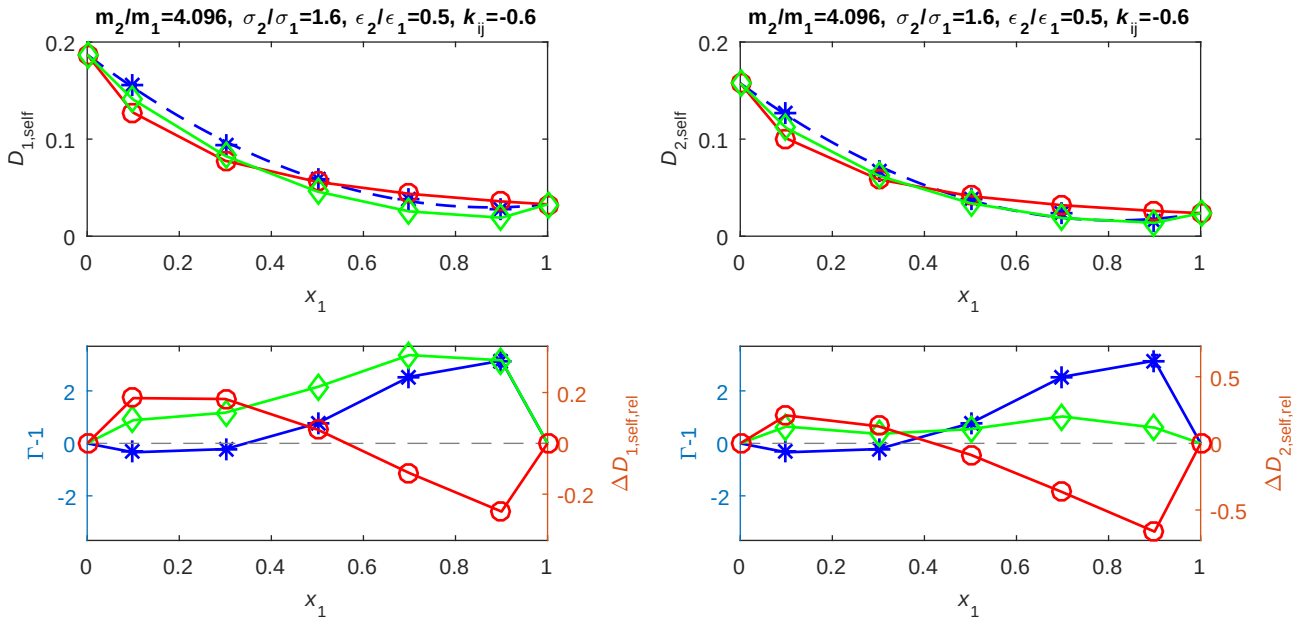

m2/m1=2.744, σ2/σ1=1.4, ϵ2/ϵ1=0.6, kij=-0.3
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=2.744, σ2/σ1=1.4, ϵ2/ϵ1=0.6, kij=-0.3
D2,self
x1
Γ-1
ΔD2,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=1, kij=0
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=1, kij=0
D2,self
x1
Γ-1
ΔD2,self,rel


m2/m1=4.096, σ2/σ1=1.6, ε2/ε1=1, kij=-0.6
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ε2/ε1=1, kij=-0.6
D2,self
x1
Γ-1
ΔD2,self,rel
m2/m1=4.096, σ2/σ1=1.6, ε2/ε1=1, kij=0.05
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ε2/ε1=1, kij=0.05
D2,self
x1
Γ-1
ΔD2,self,rel


m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=1, kij=-0.3
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=1, kij=-0.3
D2,self
x1
Γ-1
ΔD2,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=0.8, kij=0
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=0.8, kij=0
D2,self
x1
Γ-1
ΔD2,self,rel


m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=0.8, kij=-0.6
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=0.8, kij=-0.6
D2,self
x1
Γ-1
ΔD2,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=0.8, kij=-0.3
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=0.8, kij=-0.3
D2,self
x1
Γ-1
ΔD2,self,rel


m2/m1=4.096, σ2/σ1=1.6, ε2/ε1=0.6, kij=-0.6
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ε2/ε1=0.6, kij=-0.6
D2,self
x1
Γ-1
ΔD2,self,rel
m2/m1=4.096, σ2/σ1=1.6, ε2/ε1=0.6, kij=-0.3
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ε2/ε1=0.6, kij=-0.3
D2,self
x1
Γ-1
ΔD2,self,rel


m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=0.5, kij=-0.6
D1,self
x1
Γ-1
ΔD1,self,rel
m2/m1=4.096, σ2/σ1=1.6, ϵ2/ϵ1=0.5, kij=-0.6
D2,self
x1
Γ-1
ΔD2,self,rel

S2 Self-diffusion coefficients of molecular systems (experimental data)

S2.1 Relative deviations $\Delta D_{2,\mathrm{self,rel}}$ of the McCarty-Mason prediction as a function of the thermodynamic factor Γ for component 2

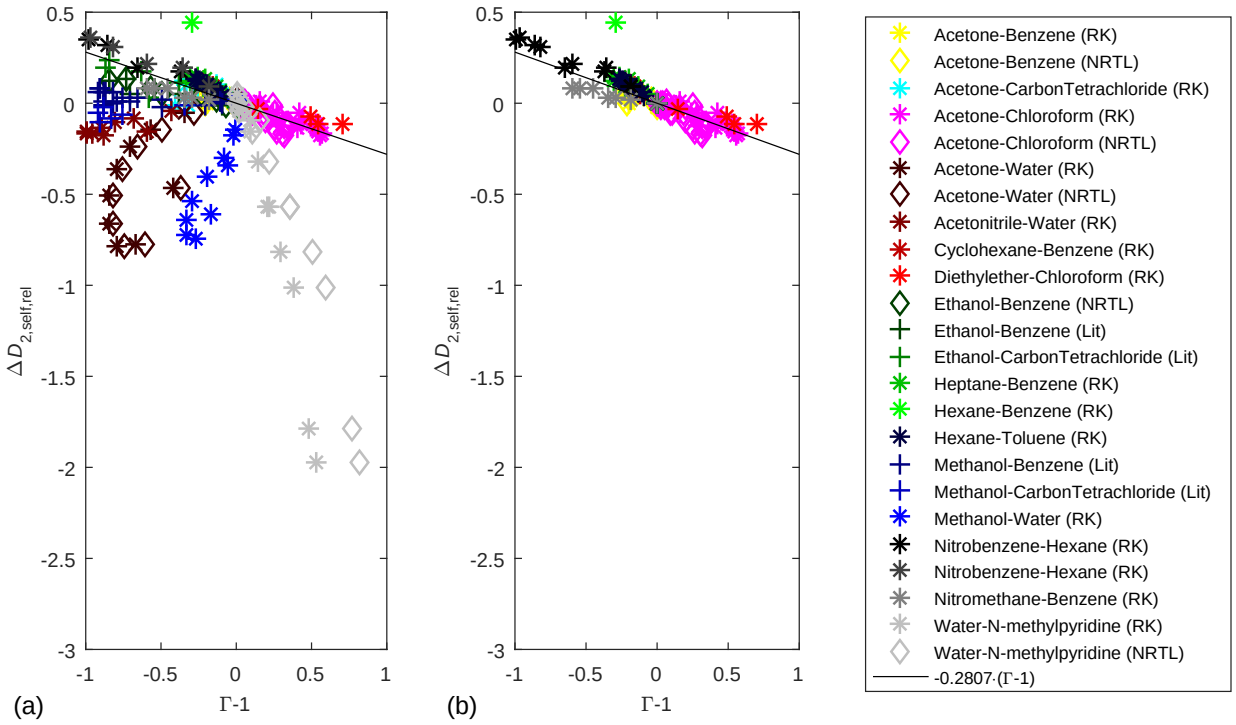
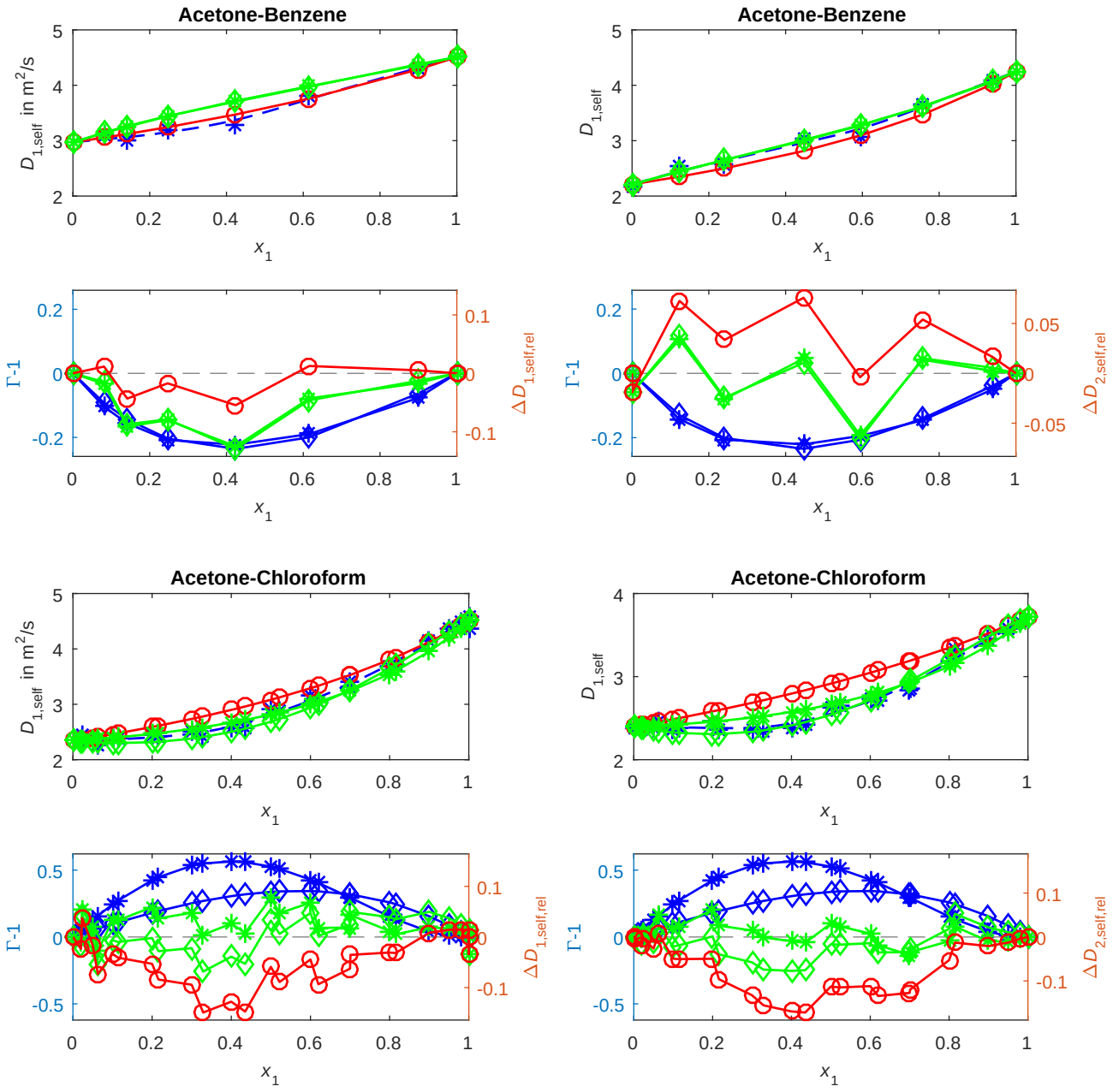
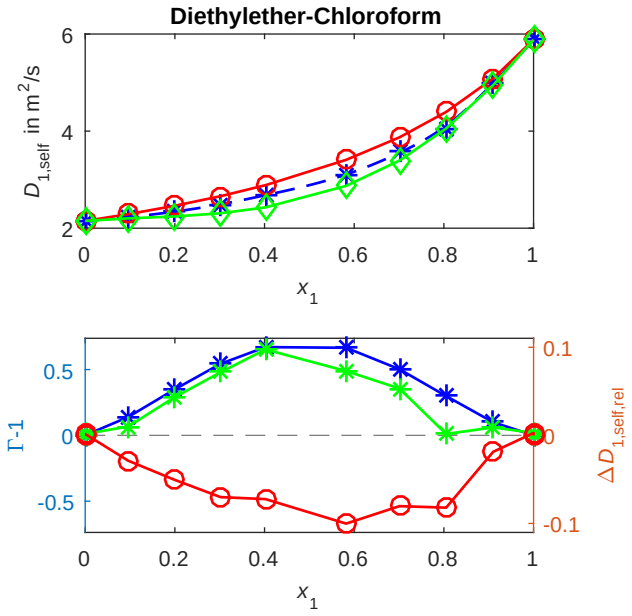
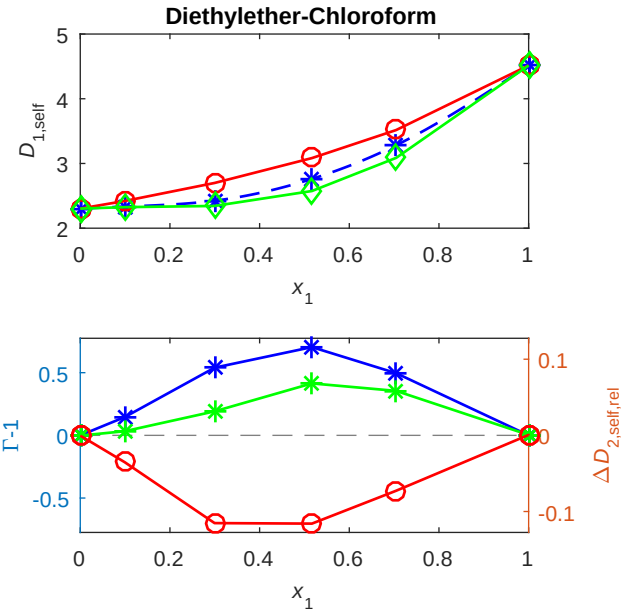


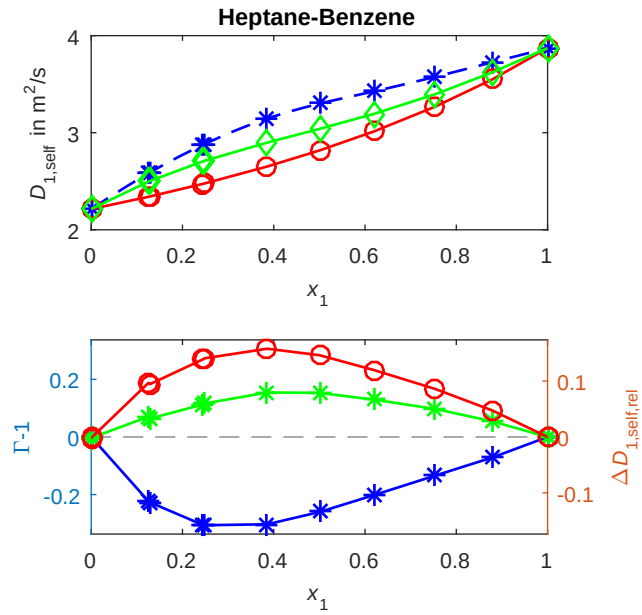
Figure S2: Relative deviations $\Delta D_{2,\mathrm{self,rel}}$ of the McCarty-Mason prediction (Equation (6)) as function of the thermodynamic factor Γ for molecular systems (symbols) and linear fit of $\Delta D_{2,\mathrm{self,rel}}$ derived from LJ systems (black line, cf. Equation (23)). Stars: Experimental data with thermodynamic factors calculated with Redlich-Kister (RK). Diamonds: Experimental data with thermodynamic factors calculated with NRTL. Plus symbols: Experimental data with thermodynamic factors reported in literature.
(a) $\Delta D_{2,\mathrm{self,rel}}$ for all considered molecular systems.
(b) $\Delta D_{2,\mathrm{self,rel}}$ for molecular systems with molar mass ratios $M_2/M_1 < 2$ and without dimerising species.

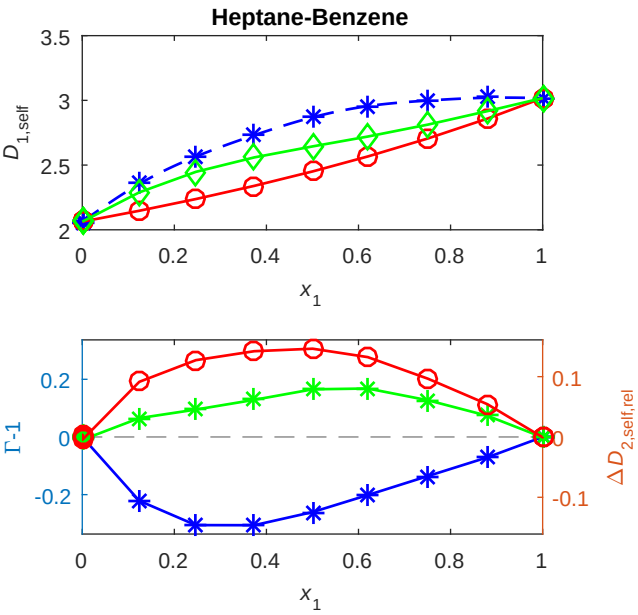
S2.2 Molecular systems with molar mass ratios $M_2/M_1 < 2$ and without dimerising species

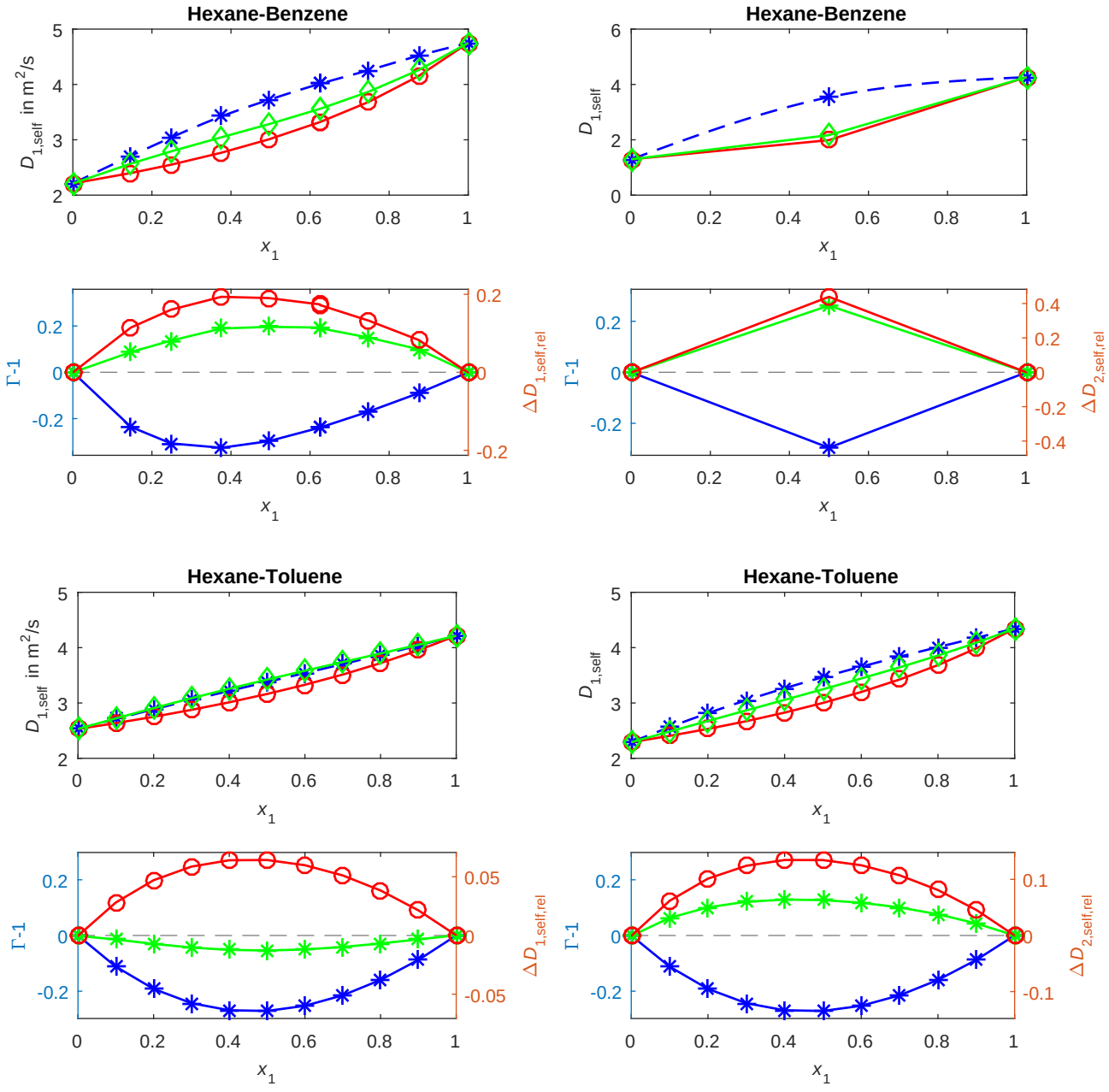


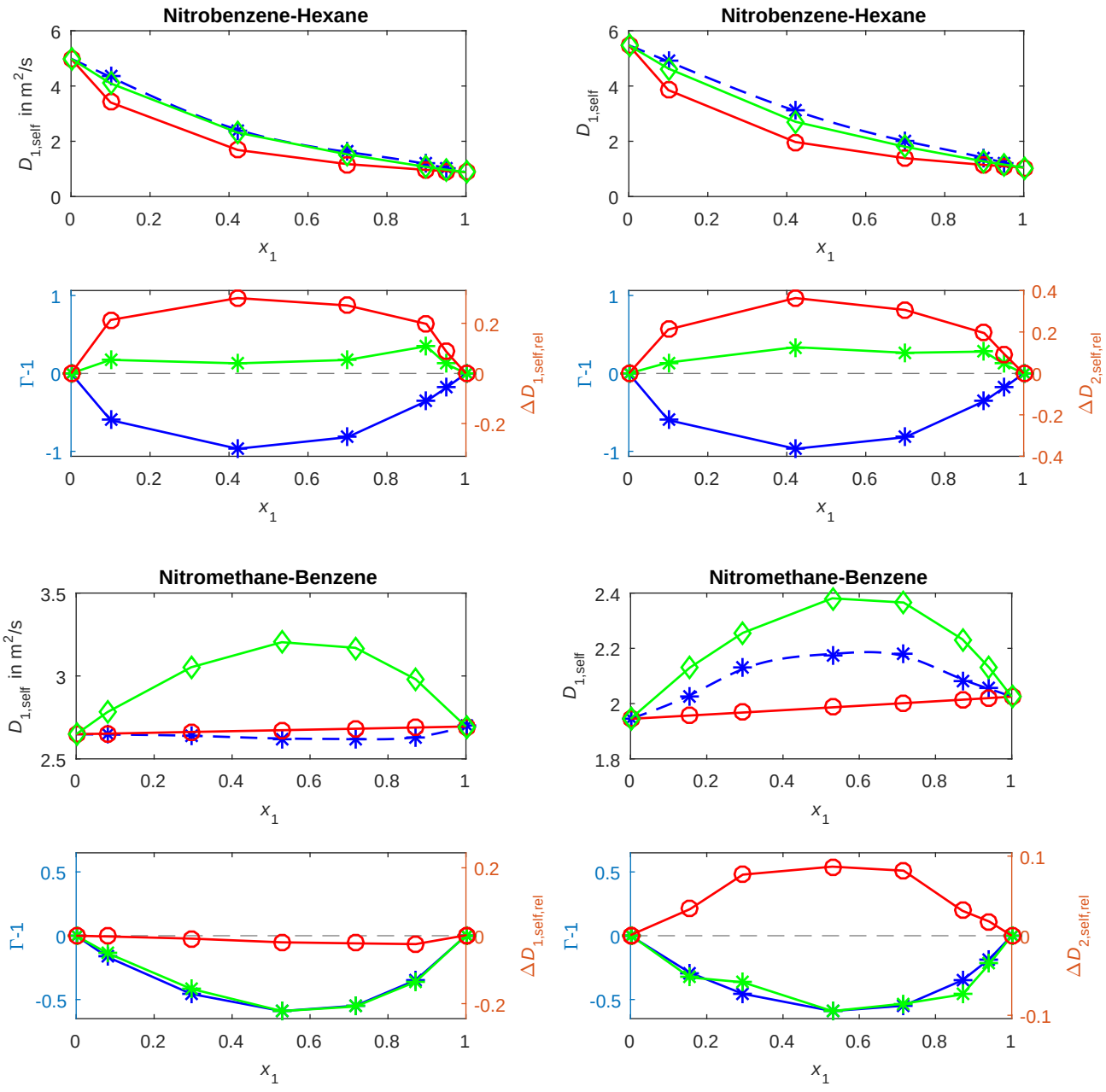

Diethylether-Chloroform
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$


Diethylether-Chloroform
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$

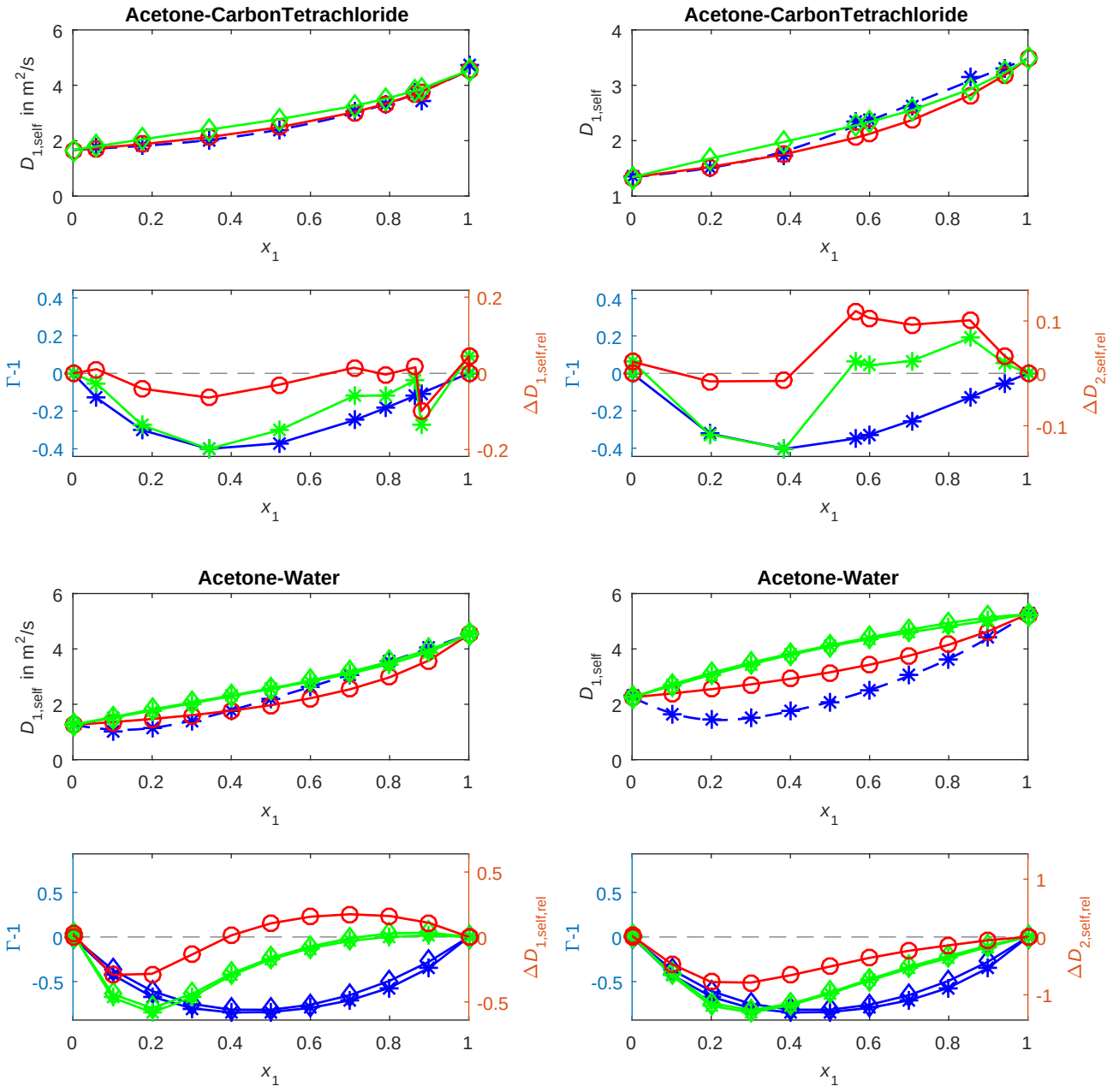

Heptane-Benzene
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$

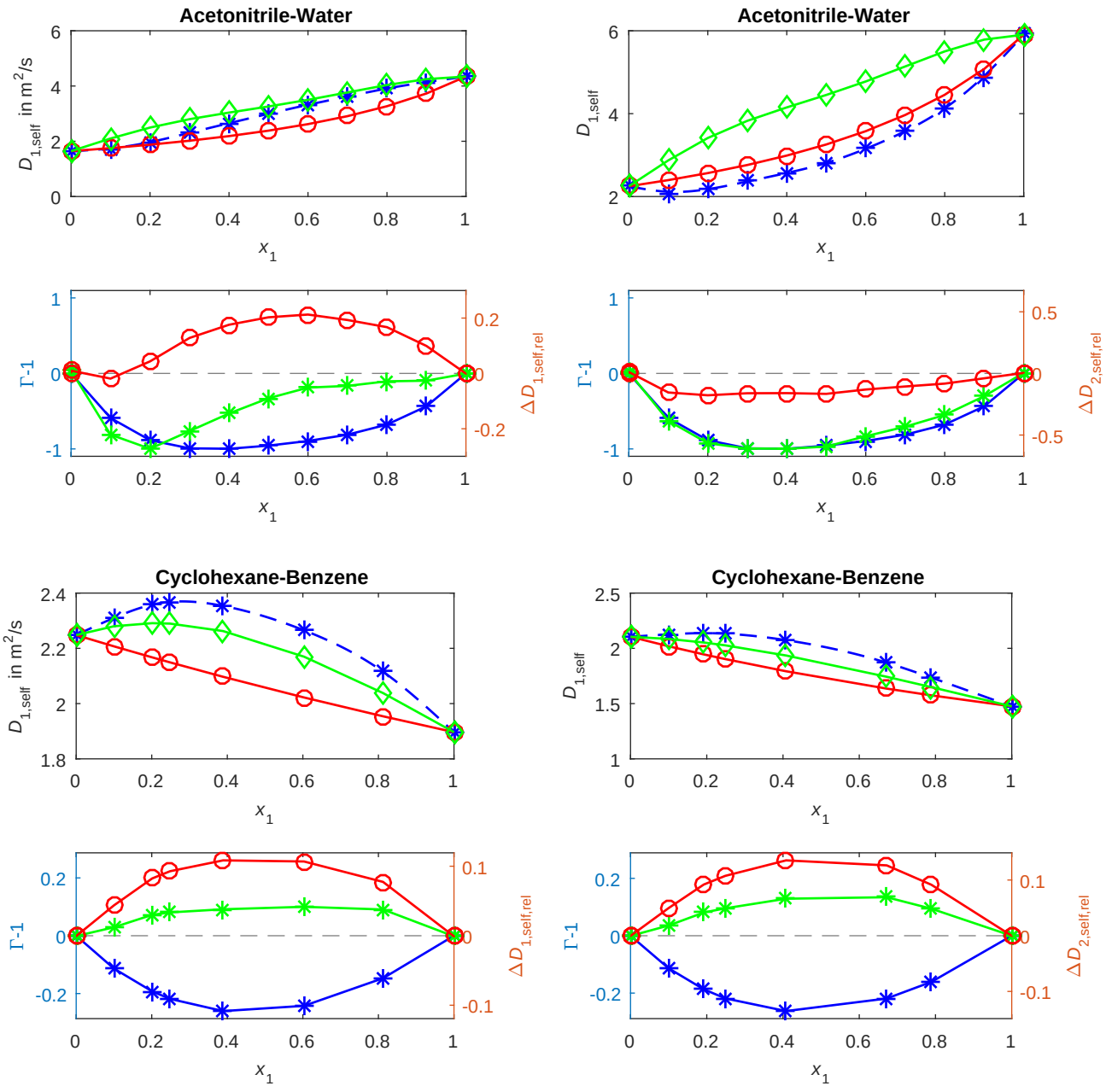

Heptane-Benzene
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$

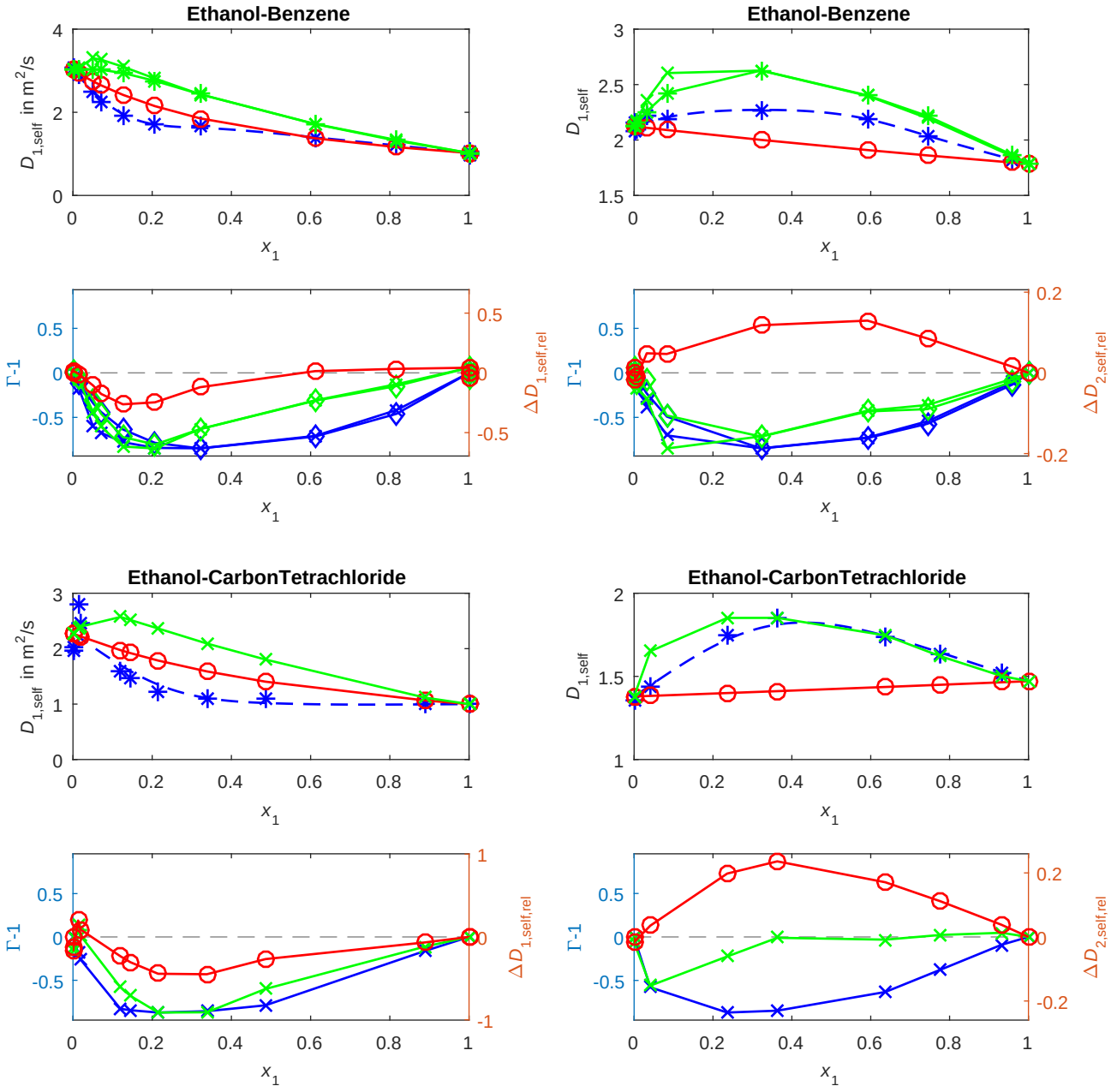

Hexane-Benzene
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Hexane-Benzene
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$
Hexane-Toluene
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Hexane-Toluene
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$

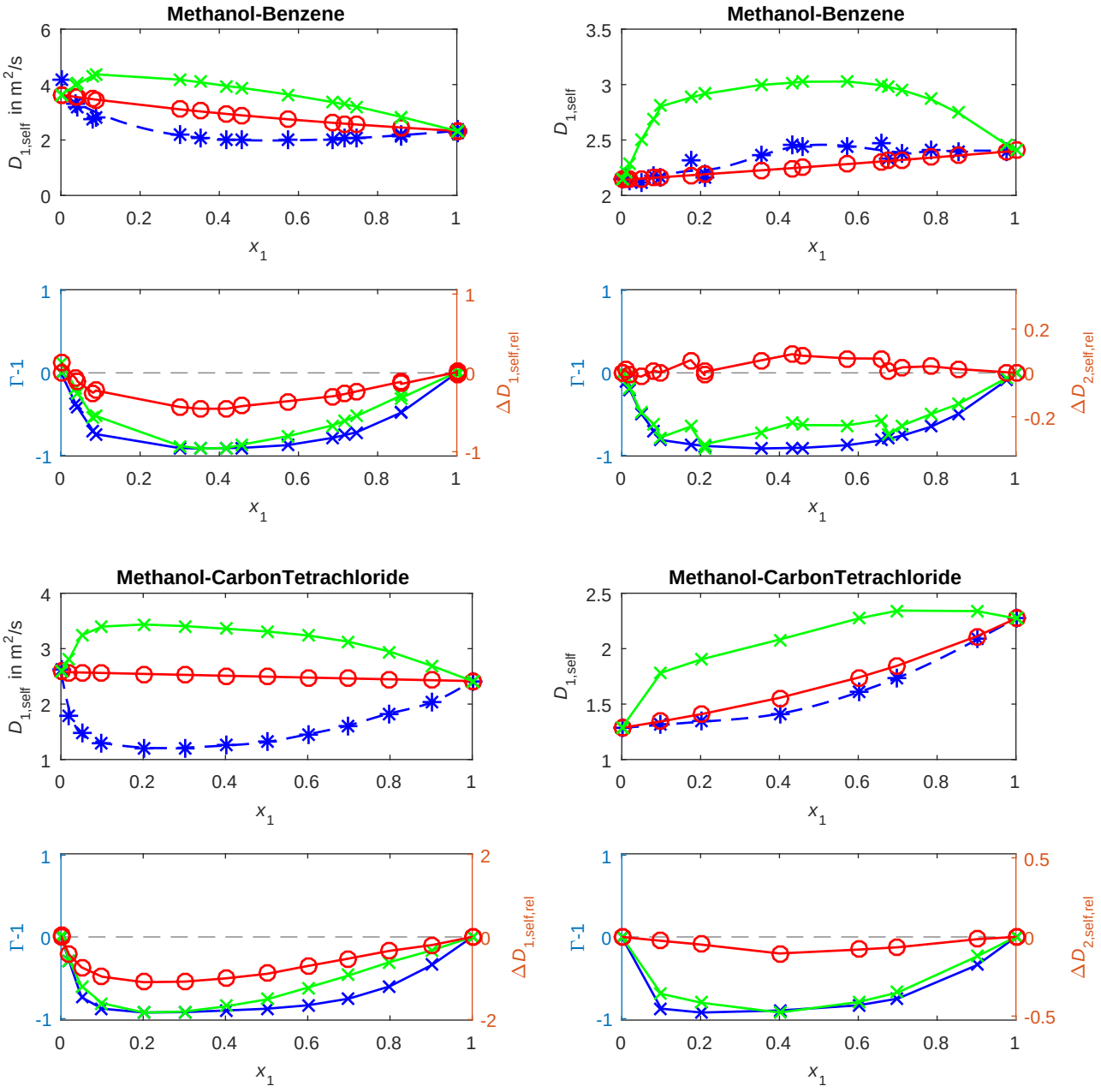

Nitrobenzene-Hexane
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Nitrobenzene-Hexane
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$
Nitromethane-Benzene
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Nitromethane-Benzene
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$

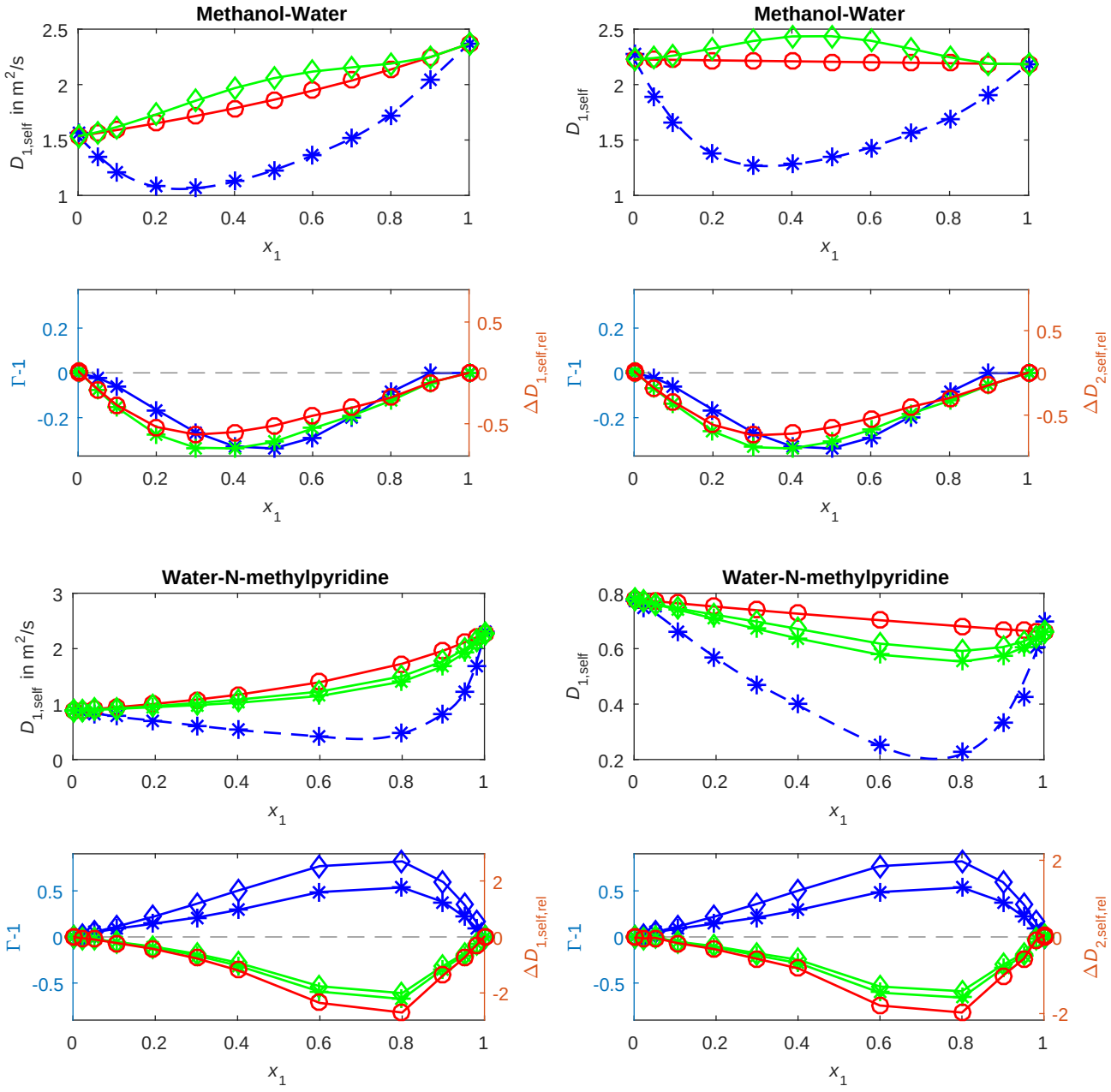
S2.3 Molecular systems with molar mass ratios $M_2/M_1 > 2$ and/or with dimerising species




Acetonitrile-Water
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Acetonitrile-Water
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$
Cyclohexane-Benzene
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Cyclohexane-Benzene
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$


Ethanol-Benzene
$D_{1,self}$ in m^2/s
x_1
Ethanol-Benzene
$D_{1,self}$
x_1
Γ-1
$\Delta D_{1,self,rel}$
x_1
Γ-1
$\Delta D_{2,self,rel}$
x_1
Ethanol-CarbonTetrachloride
$D_{1,self}$ in m^2/s
x_1
Ethanol-CarbonTetrachloride
$D_{1,self}$
x_1
Γ-1
$\Delta D_{1,self,rel}$
x_1
Γ-1
$\Delta D_{2,self,rel}$
x_1


Methanol-Benzene
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Methanol-Benzene
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$
Methanol-CarbonTetrachloride
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Methanol-CarbonTetrachloride
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$


Methanol-Water
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Methanol-Water
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$
Water-N-methylpyridine
$D_{1,self}$ in m^2/s
x_1
Γ-1
$\Delta D_{1,self,rel}$
Water-N-methylpyridine
$D_{1,self}$
x_1
Γ-1
$\Delta D_{2,self,rel}$