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THE DEVIATIONS FROM THE LAW OF MASS ACTION FOR SIMPLE BIMOLECULAR REACTIONS: MOLECULAR DYNAMICS STUDY*

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The influence of concentrations of reagents on the rate of reaction: $A + B \to C + B$ has been investigated by performing large scale computer simulations on systems of spherically symmetric molecules. The problem has been analyzed both for deterministic systems (gas, liquid) and for the stochastic ones where the particles are immersed in the Brownian medium. Significant deviations from the law of mass action have been found. The deviations result not only from fluctuations in concentrations of reagents. For the Brownian systems the simulations have given a positive value of the excess in the rate coefficient even for very long times, which contradicts with general expectations. The reason for the positive excess values is repulsion between B particles (the so called excluded volume effect). The effect is strongly influenced by the shape of the probability density function for B–B pairs. As a result, for the liquids the effect is weaker: for short times the excess in rate coefficient is positive but for long times it becomes negative.

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1. Introduction

Recent computer investigations on the influence of the concentration of B (called quencher or trap) on the rate of the reaction: $A + B \to C + B$ are presented and discussed. The reaction is an example of the so-called diffusion controlled reaction. First theory of the kinetics of the problem was proposed over 90 years ago by Smoluchowski [1]. The Smoluchowski approach [1, 2] agrees with the law of mass action, which assumes that the influence of quencher concentration, c, on the reaction rate coefficient, $k(t, c)$, can be neglected. The assumption is a rough approximation. An extreme

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example is the reaction: $A + B \rightarrow PP$ for which, according to theoretical predictions [3–6], the fluctuations and many particle effects may dramatically change the asymptotic behavior as compared to that predicted by the Smoluchowski approach. The Smoluchowski model is very simplified. Modern theories attempt to treat the problem of reaction kinetics deeper [7–11]. The theoretical works on the quencher concentration dependence effect (QCDE) for the case of reaction studied here can be also found in the literature [12–15].

Till to 2005 the problem of QCDE has drawn a very little attention of computer physics. Zhou and Szabo [16] simulated the bimolecular irreversible reaction for different c but the effect was treated only in a very qualitative way. The interactions between reactants moving in Brownian medium were also taken into account in the simulation of Senapati *et al.* [17]. First attempt to estimate the excess in $k(t, c)$ was done in 2005 [18]. Obtaining quantitative results appeared to be not easy and the simulations, performed using the standard molecular dynamics method, showed only that for the investigated liquids QCDE decreased the reaction rate in a long time limit. Further simulations have been performed by applying the method of prerecorded trajectory of Gorecki [19–21], which enabled to consider chemical systems corresponded to 10^7–10^9 particles. Many interesting results have been obtained and analyzed [21–24]. A surprising result was that the excess in the rate coefficient appeared to be positive for the whole simulation times of the Brownian systems [22] as well as for quite long times for the deterministic liquids [21, 22]. Very recent simulations [25] showed that the reason of the positive values are the interactions between B molecules.

In this paper the most important results of the simulations on QCDE are presented and discussed. Up to now, the simulation have been performed only for soft sphere systems at very selected conditions. Here, the problem is generalized by performing series of additional simulations for different potentials and thermodynamic conditions. The results are discussed and compared to the model from the previous paper [25].

2. The model and some useful formulas

The following irreversible reaction:

$$A + B \rightarrow C + B \tag{2.1}$$

for spherical molecules A, B, and C in three-dimensional bulk liquid is considered. It is assumed that the molecules are mechanically identical and differ only by the chemical properties. The reaction (2.1) is instantaneous and the reaction probability, $P(r, t)$, does not depend on position of other particles. Thus:

$$P(r,t) \; = \; \Theta(a-r)\,, \tag{2.2}$$

where r is the distance between A and B, a is the reaction radius, and $\Theta(x)$ is the Heaviside function.

The quantity obtained directly from simulations is the number of A particles as a function of time, $N_A(t)$, that gives the survival probability for A: $S(t,c) = N_A(t)/N_A(0)$ related to the rate coefficient of the reaction by:

$$S(t,c) \; = \; \exp(-c\int\limits_0^t k(t',c)dt')\,. \tag{2.3}$$

The excess in the survival probability due to a finite quencher concentration can be defined as:

$$\Delta S \; = \; S(t,c) - S_0(t,c)\,, \tag{2.4}$$

where:

$$S_0(t,c) \; = \; \lim_{c'\to 0} S(t,c')^{c/c'} \tag{2.5}$$

is the survival probability for an idealized reference system in which quencher molecules are statistically fully independent.

Simulations showed [21, 22] that both for liquids and Brownian systems the following relation holds with surprisingly high accuracy for a quite large range of c:

$$S(t,c) \; = \; S_0(t,c)\left(1 - F_c(t)c^2\right)\,, \tag{2.6}$$

where $F_c(t)$ is independent of c. According to (2.3)$-$(2.6), $F_c(t)$ is strictly correlated with the excess in $k(t,c)$:

$$\Delta k \equiv k(t,c) - k(t, c\to 0) \; = \; c\frac{\partial F_c}{\partial t}\left(1 - F_c(t)c^2\right)^{-1}\,. \tag{2.7}$$

If $F_c(t)$ is independent of c, it can be evaluated from the following formula:

$$F_c(t) \; = \; \frac{(1-R)}{c(c-Rc_0)} + O\left(F_c(t)^2 c_0^2\right)\,, \tag{2.8}$$

where

$$R = \frac{S(t,c)}{S(t,c_0)^{c/c_0}}\,.$$

Relation (2.8) is more useful than (2.6) and (2.5) since the condition $c_0 \to 0$ is not necessary. Following the derivation of (2.8) in Ref. [22] it can be seen that if c_0 is sufficiently low, the formula (2.8) can be applied with reasonably accuracy even if $F_c(t)$ depends on c. $F_c(t)$ presented in this paper are always evaluated from (2.8).

3. The setup for computer experiments

The computer simulations were performed using molecular dynamics method [26] on the systems of the total number of particles, N, enclosed in a cubic box of the volume, V. The periodic boundary conditions were applied [26]. The A, B, and C particles differed only by the chemical identify parameters and, except for the additional simulations (Section 4.3), interacted with the soft sphere potential of the following form:

$$u(r) = \begin{cases} \varepsilon[\exp(\alpha(1-r/\sigma)) - 1/3] & \text{if } r \le \sigma \\ \varepsilon(\alpha^3/12)(r_c - r/\sigma)^3\theta(r_c - r/\sigma) & \text{if } r > \sigma\,, \end{cases} \tag{3.1}$$

where $\alpha = 25.0$, ε and σ are the energy and size parameters, and $r_c = 1+2/\alpha$. All numerical values presented further are expressed in the reduced units (*i.e.* for $\sigma = \varepsilon = m = 1.0$ where m is the particle mass).

3.1. Classical simulations

Two kinds of systems were simulated: the deterministic systems (the liquid at the number density $\varrho = N/V = 0.72$ and 1.04, the gas at $\varrho = 0.0288$) and the Brownian ones ($\varrho = 0.0072 - 0.0288$). The temperature, if is not explicitly given, is always $k_{\mathrm{B}}T = 1.25$. The deterministic systems were simulated applying the molecular dynamics NVE [26] method in which the Newton equations of motion were solved by using the Verlet "leapfrog" algorithm [26,27]. In the Brownian systems the time evolution of the particle coordinates ($\boldsymbol{r}_i$, $\boldsymbol{v}_i$) were obtained from the Verlet scheme mixed with the Euler–Maruyama approximation for the stochastic term [28]. Which gives:

$$\begin{aligned} \boldsymbol{v}_i\left(t+\frac{\delta t}{2}\right) &= \boldsymbol{v}_i\left(t-\frac{\delta t}{2}\right) - \frac{\delta t}{m}\left(\sum_{j=1}^{N}\frac{\partial u}{\partial \boldsymbol{r}_{ij}} + \frac{k_{\mathrm{B}}T}{D_B}\boldsymbol{v}_i(t)\right) \\ &\quad + \vec{\xi}_i\frac{k_{\mathrm{B}}T}{m}\sqrt{\frac{2\delta t}{D_B}}\,, \qquad (3.2) \\ \boldsymbol{r}_i(t+\delta t) &= \boldsymbol{r}_i(t) + \boldsymbol{v}_i\left(t+\frac{\delta t}{2}\right)\delta t\,, \qquad (3.3) \end{aligned}$$

where: k_{B} is the Boltzmann constant, D_{B} is the diffusion constant imposed by the Brownian medium, $\vec{\xi}$ is a three dimensional random variable normally distributed, and

$$\boldsymbol{v}_i(t) = \left(\boldsymbol{v}_i\left(t-\frac{\delta t}{2}\right) + \boldsymbol{v}_i\left(t+\frac{\delta t}{2}\right)\right)\Big/2\,.$$

The time step δt was always equal to $0.01\sigma(m/\varepsilon)^{1/2}$.

During the considered chemical process the system was always in the mechanical equilibrium state. Initially, at $t = 0$, the B components were assigned to randomly selected particles. All the remaining particles were marked as A (C was absent). If at $t = 0$ the condition (2.2) was fulfilled, A was converted to C immediately and was not taken into account in the evaluation of $S(t, c)$. For $t > 0$, the reaction (2.1) was realized by relabeling A to C according to (2.2) and the condition was checked once per one time step. Usually the reaction radius $a = \sigma$. Some simulations for $a = 1.08\sigma$ have been also performed.

A crucial problem of the simulations was the accuracy of measurements [17]. The efficiency of computations has been significantly increased by applying the method of prerecorded trajectory [19–21], which benefits from the fact that the reaction (2.1) does not disturb physical evolution of the system. The method considers a chemical system build up of L^3 sub-systems obtained by translating positions of the particles of the basic N particle system L times in each of x, y, z directions. The time evolution is realized by repeating the evolution of the basic system in each of the sub-systems. The reaction (2.1) occurs in the whole system treating all the particles and their images (obtained by the translation) as real reagents. As a result, from the point of view of the chemical process, the system evolves as composed of $N \times L^3$ particles, which increases the accuracy of the "measurements" many times when compared to that for the basic system. Another advantage of the method is that the increase in the number of reagents significantly decreases the scale of a possible size effect (*i.e.* the inconsistency between the results for different number of reagents). More information on the optimization and simulation details can be found in Refs. [21, 22, 24]. The simulations described above are called further the classical simulations.

3.2. The method of parallel systems

One of the aims of the work was to determine the contributions to the excess values coming from interactions between the particles of different kinds. The classical simulations are not suitable for this purpose because the thermodynamic conditions change with changing c if A–B or/and B–B interactions are cancelled, which makes determination of the excess value impossible. New method, called the method of "parallel systems" (PS) [25], has been designed to solve the problem. The method considers the system composed of two subsystems in which A and B do not interact physically (*i.e.* for AB pairs, $u(r) \equiv 0$) but they still react chemically according to (2.1) and (2.2). A (and C) particles form the subsystem which is physically identical to the corresponding classical system. It remains physically unchanged even if one changes the number of B or even, going further, cancels B–B

interactions. This enables to determine excess values. B particles belong to the second subsystem with ϱ and T equal to that of the corresponding classical system. Most of B is assigned to be non-active (*i.e.* do not react with A) to make c identical to that of the classical system. Two cases are considered: (1) B–B interactions are the same as for the corresponding classical system. (2) B–B interactions are cancelled and the time evolution of B particles is governed by (3.2) for $u(r) \equiv 0$.

4. Results and discussion

4.1. General results

Figs. 1 and 2 show the time evolutions of $F_c(t)$ for different concentrations of B for the liquid (Fig. 1) and for the Brownian system (Fig. 2). Considering relation (2.7), the figures illustrate very surprising result [21, 22]: For the Brownian system, the excess in $k(t,c)$ is positive and, except for very short times, constant. For the liquid, the excess is positive at short times and becomes negative when t is large. The independency of $F_c(t)$ from c, which is obvious from Figs. 1 and 2, is discussed in Section 4.4.

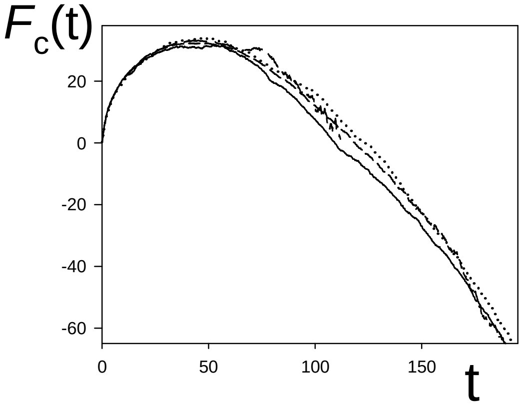

Fig. 1. $F_c(t)$ for the reaction in the liquid: $\varrho = 0.72$, $a = \sigma$. The solid line: $c = 0.0036$. The dotted line: $c = 0.0072$. The short dashed line: $c = 0.0144$. The long dashed line: $c = 0.0288$. $c_0 = 0.00045$.

Positive deviations are also seen in the excess values of the relative spatial correlations between A and B which are strongly correlated with Δk [22]. In this case the excess values have been defined as:

$$\Delta\sigma_{AB}(l,c,t) = \sigma_{AB}(l,c,t) - \sigma_{AB}(l,c_0,t)\,, \tag{4.1}$$

where:

$$\sigma_{AB}(l,c,t) = \frac{\langle n_A(t)n_B(t)\rangle_l}{\langle n_A(t)\rangle_l\langle n_B(t)\rangle_l} - 1$$

$\langle n_A(t)\rangle_X$ is current number of the X particles enclosed in an imaginary cell of the box-length l, $\langle\rangle_l$ is the spatial average over the cell, and c_0 is sufficiently low to make the definition (4.1) reasonable.

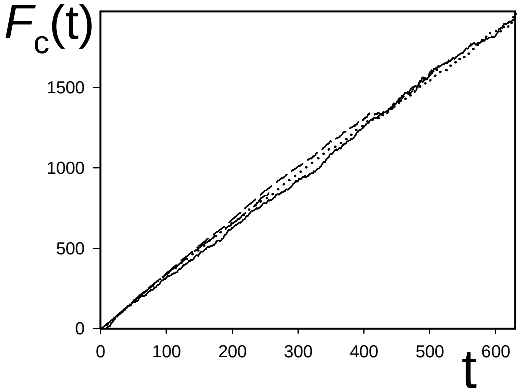

Fig. 2. $F_c(t)$ for the Brownian system: $\varrho = 0.0288$, $a = \sigma$. The solid line: $c = 0.0018$. The dotted line: $c = 0.0036$. The short dashed line: $c = 0.0072$. The long dashed line: $c = 0.0144$. $c_0 = 0.00045$.

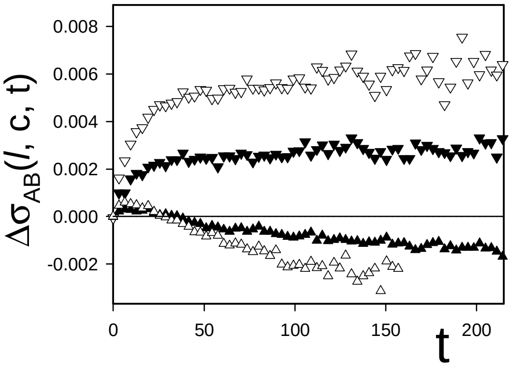

Fig. 3. Excess in $\sigma_{AB}(l,c,t)$ for the liquid (as in Fig. 1; the triangles up) and the Brownian system (as in Fig. 2; the triangles down). The filled symbols: $c = 0.0072$. The empty symbols: $c = 0.0144.l \cong 4.93$.

The values of $\Delta\sigma_{AB}(l,c,t)$ as a function of t for the Brownian system and for the deterministic liquid are presented in Fig. 3. The correlation between $\partial F_c/\partial t$ ($\cong \Delta k/c$) from Figs. 1, 2 and $\Delta\sigma_{AB}(l,c,t)/c$ from Fig. 3 is evident. The only small inconsistency is that the time when $\Delta\sigma_{AB}(l,c,t)=0$ for the liquid does not match exactly with that of the maximum of $F_c(t)$ in Fig. 1.

4.2. The reason for the positive excess values

The results form Figs. 1–3 are quite strange since the fluctuations in concentration are generally expected to make both Δk and $\Delta\sigma_{AB}(l,c,t)$ negative. The results presented in Figs. 4 and 5 clearly show that the reason of the positive excesses in the rate coefficient are *B*–*B* interactions. The figures compare $F_c(t)$ from classical simulations (as in Figs. 1 and 2) with that from the PS method (both for *B*–*B* interactions active and cancelled). Both in Fig. 4 and in Fig. 5 the *B*–*B* interactions strongly influence the excess values. If they are absent (*i.e.* *B* particles move in space in a fully independent way) both $F_c(t)$ and Δk (from (2.7)) are significantly negative for all the range of time (the dash-dotted lines in Figs. 4 and 5). The influence of *A*–*B* interactions is very weak. For the Brownian system (Fig. 5), it is evident. For the liquid (Fig. 4), the cancellation of *A*–*B* interactions only shifts $F_c(t)$. Except for very short times, $\partial F_c/\partial t$ for *B*–*B* interactions active (the dashed line in Fig. 4) remains very close to that obtained from the classical simulations. The shift is probably caused by a high difference in initial distribution of *A* around *B* between the systems with *A*–*B* interactions cancelled and active. For the Brownian system $\varrho = 0.0288$ and the differences is much lower.

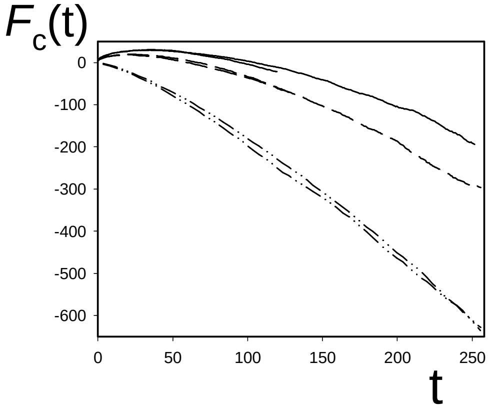

Fig. 4. $F_c(t)$ for the liquid: $\varrho = 0.72$, $a = 1.08\sigma$. The solid lines: the classical simulations ($c = 0.0072$ and 0.0144). The dashed lines: the PS simulations for *B*–*B* interactions active ($c = 0.0072$ and 0.0144). The dash-dotted lines: the PS simulations for *B*–*B* interactions cancelled ($c = 0.0036$ and 0.0144). $c_0 = 0.0009$.

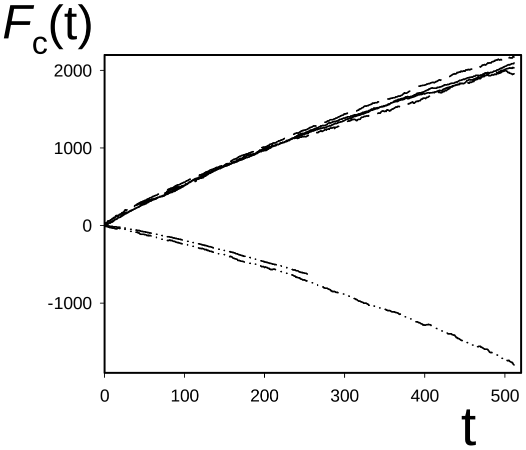

Fig. 5. $F_c(t)$ for the Brownian system: $\varrho = 0.0288$, $a = 1.08\sigma$. The solid lines: the classical simulations ($c = 0.00135$ and 0.0036). The dashed lines: the PS simulations for B–B interactions active ($c = 0.0018$ and 0.0036). The dash-dotted lines: the PS simulations for B–B interactions cancelled ($c = 0.0018$ and 0.0072). $c_0 = 0.000225$.

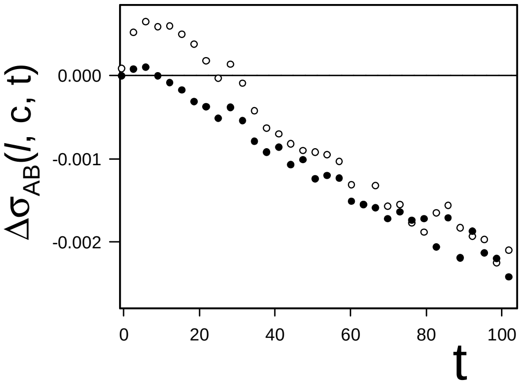

Fig. 6. Excess in $\sigma_{AB}(l, c, t)$ for the liquid: $\varrho = 0.72$, $a = 1.08\sigma$, $c = 0.0144$. $l \cong 4.93$. The empty circles — the PS simulations for B–B interactions active. The filled circles: the PS simulations for B–B interactions cancelled.

B–B interactions significantly influence also fluctuations in concentrations. This is evident from Fig. 6 that compare $\Delta\sigma_{AB}(l, c, t)$ for the liquid in the absence of A–B interactions for B–B interactions active and non-active. Cancellation of B–B interactions makes $\Delta\sigma_{AB}(l, c, t)$ negative for almost all t (the filled circles in Fig. 6). The influence of A–B interactions is much weaker. This can be seen comparing Fig. 6 to Fig. 3. If B–B interactions are active (the empty circles in Fig. 6), the dependence of $\Delta\sigma_{AB}(l,c,t)$ on t is qualitatively very close to the corresponding curves in Fig. 3 (the triangles up).

The influence of B–B interactions on $\Delta\sigma_{AB}(l,c,t)$ and on Δk has been discussed in Ref. [25]. The main conclusion is that the effect is a result of the excluded volume effect: because of the B–B repulsion the B particles are distributed more and more regularly with increasing c. This results in positive contributions to $\Delta\sigma_{AB}(l,c,t)$ as well as to Δk. The increase in Δk can be very simply interpreted physically: the more regular distribution of B the more effective the reaction is. But the effect is not only a result of simple excluded volume effect. The details of the liquid structure, here the shape of the conditional probability density for B–B pair $g_{BB}(r)$, have significant influence on the strength of the effect. This is seen when considering the model from Ref. [25]. The model bases on the superposition approximation and is in analogy to that of Jung and Lee [29] for the reaction $A+B\rightarrow PP$. It predicts that the time evolution of the conditional probability density for A–B pair $g_{AB}(r,t)$ fulfills, under some simplifications, the following equation:

$$\frac{\partial g_{AB}}{\partial t} = D_\Sigma \nabla^2 g_{AB}(r,t) + 4a^2 c\sqrt{\pi k_{\mathrm{B}}T/m}\,R(a,t)\,g_{AB}(r,t)\,g_{AB}(a,t)\,, \tag{4.2}$$

where: $r>a$, ∇^2 is the Laplacian, D_Σ is the sum of the diffusion constants for A and B,

$$R(a,r) = 1-\frac{1}{4\pi a^2}\int g_{BB}(|\boldsymbol{r}'-\boldsymbol{r}|)\,\delta(r'-a)\,d\boldsymbol{r}' \tag{4.3}$$

and the radiation boundary condition as in the work of Zhou and Szabo [16] is applied.

The model is very simplified, but it predicts an important property of the effect discussed here. According to (4.2), the B–B interactions influence $g_{AB}(r,t)$ by deviating $R(a,r)$ from 0. As a consequence, according to (4.3), the presence of the region of strong repulsion and low probability density for $r<\sigma$ can be at least partly compensated by the increase in the mean probability for $r>\sigma$. Usually a is very close to σ. Therefore, for dense fluids, first of all because of a sharp maximum in $g_{BB}(r)$ for r just above σ, the effect should be significantly weaker than for the Brownian systems, for which $g_{BB}(r)$ can be roughly approximated by $\theta(r-\sigma)$. In general, from the stochastic point of view, the factor of interest is the probability density averaged adequately over all the space but not only that for $r<a$. This is in full agreement with the simulations: the difference between $\partial F_c/\partial t$ at high t for B–B interactions active and cancelled is significantly higher for

the Brownian system (Fig. 5) than for the liquid (Fig. 4). Since the effect is not only a result of the excluded volume it is called further the generalized excluded volume effect (GEVE).

4.3. Additional test

The potential (3.1) is purely repulsive. It is a priori possible that some of the results presented above are only a consequence of this property. In order to generalize the presented results, we have performed extra simulations for two interparticle potentials with an attractive term:

$$u(r) = \begin{cases} \exp(25(1-r)) - 1.5/r^6 & \text{if } r \le r_s \\ (\Delta r^3(a_1\Delta r^2 + a_2\Delta r + a_3)\theta(r_c - r) & \text{if } r > r_s \end{cases}, \tag{4.4}$$

$$u(r) = \begin{cases} 4[\exp(18(1-r)) - 1/r^6] & \text{if } r \le R_S \\ (\Delta r^3(b_1\Delta r^2 + b_2\Delta r + b_3)\theta(r_c - r) & \text{if } r > r_c \end{cases}, \tag{4.5}$$

where $\Delta r = r - r_c$ and a_i, b_i were adjusted as to make the second derivative of $u(r)$ continues for all r. Two sets of cut-off parameters r_s and r_c were used. The short range potential for $r_s = 1.4$, $r_c = 1.65$ and the long range potential for $r_s = 1.9$, $r_c = 2.25$.

The simulations were performed for different thermodynamic conditions. The conditions and simulation results are presented in Table I. The simulation points S1 and S3 present the results from previous simulations [21, 22]. The remaining points (S2 and S4-S10) have been obtained form the classical NVE simulations for $N \times L^3 = 216000 \times 216$ and $a = \sigma$. Minimum two values of c have been considered for each point: $c_0 = 0.00125\varrho$ and $c = 0.01\varrho$. The resulted $F_c(t)$ curves were always qualitatively identical to that from Fig. 1. For S5 and S8, the simulations for two extra values of c (0.02ϱ and 0.04ϱ) have been performed and any dependence of $F_c(t)$ on c has not been noticed. The short range potentials were used, except for S5L and S8L for which the long range potentials were applied. The value of diffusion constant, D, was determined using the Einstein formula [26]. Table I gives also the parameters of the $F_c(t)$ curves: the value of Dt that $F_c(t) = 0$ (denoted as $Dt[0]$) and the maximum value of $F_c(t)$ (denoted as $\mathrm{Max}(F_c)$). The relative error of these values should not exceed 0.1. The last column presents the excess in the rate coefficient from the model ((4.2), (4.3)) at $Dt = 10.0$, Δk_{mod}, obtained using the procedure described in Ref. [25].

The most important conclusion from the simulations is that the change of $u(r)$ as well as of the thermodynamic parameters did not influence, qualitatively, the properties of $F_c(t)$. The values of $Dt[0]$ and $\mathrm{Max}(F_c)$ from Table I enables us also to derive some conclusions on the influence of the potential shape and of the thermodynamic parameters on the "strength" of GEVE. However, $Dt[0]$ and $\mathrm{Max}(F_c)$ are a result of both GEVE and the

TABLE I

	$u(r)$	ϱ	$k_{\mathrm{B}}T$	D	$Dt[0]$	$\mathrm{Max}(F_c)$	$\Delta k_{\mathrm{mod}}/c$
S1	(3.1)	0.72	1.25	0.158	19.0	33.	0.55
S2	(3.1)	0.80	1.25	0.112	10.1	27.	0.38
S3	(3.1)	1.04	1.25	0.023	4.5	11.	0.06
S4	(3.1)	0.72	1.00	0.133	20.2	34.	0.50
S5	(4.4)	0.72	1.25	0.158	15.5	30.	0.50
S5L	(4.4)	0.72	1.25	0.161	15.0	27.	0.51
S6	(4.4)	0.80	1.25	0.115	11.8	30.	0.37
S7	(4.4)	0.72	1.00	0.132	12.9	25.	0.45
S8	(4.5)	0.72	1.25	0.097	15.8	27.	0.32
S8L	(4.5)	0.72	1.25	0.107	16.5	26.	0.33
S9	(4.5)	0.80	1.25	0.061	8.5	22.	0.20
S10	(4.5)	0.72	1.00	0.073	15.1	24.	0.20

fluctuations in concentration, but some approximate qualitative conclusions are possible since the fluctuations "strength" should be less sensitive to the changes in $u(r)$ and the thermodynamic conditions than GEVE is. Table I clearly shows that the strength of the effect mainly depends on the density and decreases with increasing ϱ (S1-S3, S5-S6, S8-S9). The influence of the temperature is much weaker. Considering the simulation errors, only for the potential (4.4) some low decrease in both $Dt[0]$ and $\mathrm{Max}(F_c)$ with decreasing $k_{\mathrm{B}}T$ is observed. This is in full agreement with the form of (4.3). An increase in ϱ increases both the first maximum in $g_{BB}(r)$ and the values of $g_{BB}(r)$ for $r < a$ (here, $a = \sigma$), which results in a significant decrease of $|R(a,r)|$. A decrease in $k_{\mathrm{B}}T$ increases the first maximum but decreases $g_{BB}(r)$ for $r < a$ and the cumulative result is much lower. The influence of the potential range (S5-S5L, S8-S8L) is completely negligible since the changes in r_s and r_c have a very low influence on $g_{AB}(r)$. Table I shows also a decrease in the strength of GEVE with changing $u(r)$ from the purely repulsive (3.1) to the attractive ones (4.4) and (4.5) (compare S1 to S5 and S8). Taking in to account (4.3), this is in full agreement with our expectations. It is also worthy to note, a strong qualitative correlation between $Dt[0]$ and Δk_{mod} for a given form of $u(r)$ (it fails only when compared S10 to S8 and S9). The correlation suggests that the model (4.2) may be a good first step for theoretical description for the process.

4.4. A comment on the independency of $F_c(t)$ from c

$F_c(t)$ from figures 1 and 2 is independent (to the accuracy of simulation errors) of the concentration of B. The independency has been fully confirmed by the simulations S5 and S8 presented in Section 4.3. Relation (2.6) is in accordance, to $O(c^3)$, with the density expansion for the time dependence of

$S(t,c)$ of diffusing particles in the presence of randomly distributed diffusing traps [30]. But the highest values of c considered here are not small (0.0288 for the liquid and 0.0144 for the Brownian system), which suggests that the formula (2.8) is not only a simply expansion to $O(c^3)$.

The property does not hold for the gas. A possible reason is that for the gas state the nature of the excess is more complex. In a general case one can write:

$$\frac{1}{c}\Delta k = J_G + J_U \,,$$

where J_G and J_U are the contributions from the excesses in the conditional probability density and in the excess in relative velocity of A towards B, respectively. More information is given in Ref. [23] (in the relation (2.7) in the cited paper the factor $1/c$ has been missed, by mistake). The simulations presented there showed that, except for one case, both for the liquid and for the Brownian systems J_U was negligible. J_U was noticeable (however still less important than J_G) only for the liquid at low density (where the relaxation is not very fast) and $a = \sigma$. Contrary to the non-gas systems, $|J_U|$ for the gas was not lower than $|J_G|$. On the other hand, according to Fig. 3 from Ref. [23], $\Delta\sigma_{AB}(l,c,t)/c$ for the gas behaves very similar to that for the Brownian systems (upper curves in Fig. 3 presented here) and is also independent of c. This suggests that, the independence of $F_c(t)$ from c is a property of J_G. For the gas, $\partial F_c/\partial c$ is non-zero because of a high value of J_U.

5. Summary

Recent results of molecular dynamics simulations on the influence of the quencher concentration on the rate of reaction (2.1) have been presented and discussed. An important result was that Δk appeared to be positive for the whole simulation times of the Brownian systems [22] (Fig. 2) as well as for quite long times for the deterministic liquids [21, 22] (Fig. 1). The positive deviations were also noted in $\Delta\sigma_{AB}(l,c,t)$ [22] (Fig. 3), which is strongly correlated with Δk. The effect has been explained using the method of parallel systems [25] that enabled to investigate the influence of interactions between molecules of given kinds on the excess values. It was shown that the positive excess values are a result of the interactions between B molecules [25] (Figs. 4–6). An important factor of the effect is the interparticle repulsion (the excluded volume effect), which results in the positive contributions. However, the influence of the liquid structure can not be neglected. For the liquid the increase in Δk is significantly weaker than for the Brownian systems (compare Fig. 4 to 5), which has been interpreted, using the model (4.2), (4.3), as a consequence of the difference in the liquid structures between the two systems.

The problem of QCDE has been generalized by performing additional simulations for different interparticle potentials and at different thermodynamic conditions. The generalized excluded volume effect (GEVE) gives a significant contribution to the excess values for different potentials ((3.1), (4.4), (4.5)) at varying temperatures and densities (Table I). No qualitative changes in $F_c(t)$ is noted. The property of $F_c(t)$ to be independent of c has been fully confirmed also for the potentials (4.4) and (4.5). The strength of GEVE significantly decreases with increasing ϱ. The influence of another factors is much weaker. This agrees with the form of (4.3). The values of $Dt[0]$ and $\mathrm{Max}(F_c)$ for a given $u(r)$ are surprisingly good qualitatively correlated with Δk_{mod} obtained from (4.2) and (4.3). This shows that the model, in spite of its simplicity, brings us an important information about the physics of the problem. This also confirms the validity of the considerations about the role of the liquid structure for QCDE.

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