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# The influence of quencher concentration on the excess in the rate of quenching reaction: molecular dynamics study

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## Abstract

Molecular dynamics simulations of the reaction  $A + B \rightarrow C + B$  for identical soft spheres in three dimensions have been performed to study the influence of the concentration of B (quencher) on the reaction rate. Many interesting results have been found. For the deterministic systems (liquid and gas), an increase in the quencher concentration decreased the reaction rate coefficient,  $k(t)$ , in the long-time limit but it increased  $k(t)$  at short times. For the Brownian systems the excess in  $k(t)$  was positive and, except for very short times, constant. Both for the liquids and the Brownian systems the excess in relative spatial correlations between reagents was strongly correlated with the excess in  $k(t)$ . The long-time behaviour of the excess in  $k(t)$  for the gas was qualitatively similar to that for liquids but the origin of the phenomenon was not the same. For the gas, the excess in  $k(t)$  was mainly caused by the excess in the mean radial velocity between A and B, which was completely negligible for the dense liquid and the Brownian system.

## 1. Introduction

In this paper recent computer investigations on the phenomenon of the influence of the concentration of B (called quencher or trap) on the rate of the reaction  $A + B \rightarrow C + B$  are presented and discussed. The reaction is an example of the so-called diffusion controlled reaction. The first theory of the kinetics of the problem, the Smoluchowski approach [1, 2], assumed that the influence of quencher concentration on the reaction rate coefficient can be neglected. Modern theories [3–8] take the influence of the quencher–quencher interactions into account. Theoretical works on the quencher concentration dependence effect (QCDE) for the case of reaction studied here can be also found in the literature [9–11]. But the theories are simplified since the problem of the QCDE is very complex. One of the questions is the role

of fluctuations. According to theoretical predictions for some reaction schemes [12–15] the fluctuations and many particle effects may dramatically change the asymptotic behaviour as compared to that predicted by the Smoluchowski approach.

Computer simulations are a good tool to model diffusion-controlled reactions but the problem of the QCDE has drawn very little attention. Zhou and Szabo [16] simulated the bimolecular irreversible reaction for different concentrations of quencher but the effect was treated only in a very qualitative way. The interactions between reactants moving in a Brownian medium were also taken into account in the simulation of Senapati *et al* [17].

The problem of the QCDE was attacked by computer simulations for the first time in 2005 [18]. Obtaining quantitative results appeared to be not easy and the first simulations, performed using the standard molecular dynamics method, showed only that for the investigated liquids the QCDE decreased the reaction rate in the long-time limit. Further simulations have been performed by applying the method of prerecorded trajectory of Gorecki [19–21], which enabled one to consider chemical systems corresponding to  $10^7$ – $10^9$  particles. Many interesting and surprising results have been obtained and analysed [21–23]. The most important of the results and the simulation method are presented and discussed in this work.

## 2. The model and some useful formulae

The following irreversible reaction



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 in their chemical properties. The reaction (2.1) is instantaneous and the reaction probability,  $p(r, t)$ , does not depend on the position of other particles. Thus

$$p(r, t) = \begin{cases} 1 & \text{if } r \leq a \\ 0 & \text{if } r > a \end{cases} \quad (2.2)$$

where  $r$  is the distance between A and B and  $a$  is the reaction radius.

The quantity obtained directly from simulations is the number of A particles as a function of time,  $N_A(t)$ , that gives the surviving probability for A:

$$S(t, c) = N_A(t)/N_A(0). \quad (2.3)$$

$S(t, c)$  is related to the rate coefficient of the reaction,  $k(t, c)$ , by

$$S(t, c) = \exp\left(-c \int_0^t k(\tau, c) d\tau\right). \quad (2.4)$$

Because of random errors inherent in simulations, it is more useful to analyse the results not with  $k(t, c)$  but with its value averaged over the time interval  $\Delta t$ :

$$\langle k(t, c) \rangle_{\Delta t} \equiv \frac{1}{\Delta t} \int_{t-\Delta t/2}^{t+\Delta t/2} k(\tau, c) d\tau = \frac{\ln(N_A(t - \Delta t/2)/N_A(t + \Delta t/2))}{c \Delta t}. \quad (2.5)$$

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

$$\Delta S = S(t, c) - S_0(t, c) \quad (2.6)$$

where:

$$S_0(t, c) = \lim_{c' \rightarrow 0} (S(t, c')^{c/c'}). \quad (2.7)$$

Since A, B and C are mechanically identical,  $\Delta S$  can be obtained by comparing the systems characterized by the same number density,  $\rho$ , and temperature,  $T$ , and differing only in the concentrations of reagents. It is useful to define the function  $F_c(t)$ :

$$S(t, c) = S_0(t, c)(1 - F_c(t)c^2). \quad (2.8)$$

The above 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 [24].

According to equations (2.4) and (2.8),  $F_c(t)$  is strictly correlated with the excess in  $k(t, c)$ :

$$\Delta k \equiv k(t, c) - k(t, c \rightarrow 0) = c \frac{\partial F_c}{\partial t} (1 - F_c(t)c^2)^{-1}. \quad (2.9)$$

The value of  $F_c(t)$  can be evaluated from the following formula:

$$F_c(t) = \frac{1 - R}{c(c - c_0 R)} + O(F_c(t)^2 c_0^2) \quad (2.10)$$

where

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

Relation (2.10) is more useful than (2.8) and (2.7) since the condition  $c_0 \rightarrow 0$  is not necessary.

### 3. The setup for computer experiments

The computer simulations were performed using a molecular dynamics method [25] on systems of the total number of particles,  $N$ , enclosed in a cubic box of the volume,  $V$ . Periodic boundary conditions were applied [25]. The A, B, and C particles differed only in their chemical identification parameters, and interacted with the soft sphere potential of the following form:

$$u(r) = \begin{cases} \varepsilon[\exp(\alpha(1 - r/\sigma)) - 1/3] & \text{for } r/\sigma \leq R_S = 1.0 \\ \varepsilon(\alpha^3/12)(r/\sigma - R_C)^3 & \text{for } R_S < r/\sigma \leq R_C = R_S + 2/\alpha \\ 0 & \text{for } r/\sigma > R_C \end{cases} \quad (3.1)$$

where  $\alpha = 25.0$ ,  $\varepsilon$  and  $\sigma$  are the energy and size parameters. A crucial property of the above potential is that it enables very fast evaluation of interparticle forces. For liquids, the computation time for a given  $N$  has been reduced over three times when compared to the previous simulations [18] in which the cut-off distance of the potential used was  $1.65\sigma$ . This allowed for a significant increase in the accuracy of ‘measurements’. For  $r/\sigma < R_S$  the potential (3.1) is very strongly repulsive so, especially for low and moderate densities, one can expect the obtained liquid structure to be similar to hard sphere ones. This may be important for the interpretation of results and, first of all, for possible further analytical works. The mathematical form of (3.1) and the relationship  $R_C = R_S + 2/\alpha$  make  $\partial u/\partial r$  differentiable for all  $r$ . The value of  $R_S$  (here, equal to 1.0) determines the border of the strong repulsion and  $\sigma R_C$  is the cut-off distance. 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).

Most of the simulations were performed for  $a = \sigma$ , which, according to (3.1), corresponded to a non-zero value of the activation energy. The case when the energy was 0 (i.e.  $a/\sigma = R_C = 1.08$ ) was also considered.

Two kinds of system were simulated: deterministic systems (both liquid and gas) and Brownian ones. The deterministic systems were simulated by applying the classical molecular dynamics  $NVE$  [25] method in which the Newton equations of motion were solved by using the Verlet ‘leapfrog’ algorithm [25, 26]. In the Brownian systems the time evolution of the

particle coordinates ( $\mathbf{r}_i$ ,  $\mathbf{v}_i$ ) were obtained from the Verlet scheme [25, 26] mixed with the Euler–Maruyama approximation for the stochastic term [27]. The resulting procedure was

$$\mathbf{v}_i(t + \delta t/2) = \mathbf{v}_i(t - \delta t/2) - \frac{\delta t}{m} \left( \sum_{i=1}^N \frac{\partial u(r_{ij})}{\partial \mathbf{r}_{ij}} + \frac{k_B T}{D_B} \mathbf{v}_i(t) \right) + \bar{\xi}_i \frac{k_B T}{m} \sqrt{2\delta t/D_B} \quad (3.2)$$

$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t + \delta t/2)\delta t$$

where  $D_B$  is the diffusion constant imposed by the Brownian medium,  $\bar{\xi}_i$  is a three-dimensional random variable normally distributed,  $k_B$  is the Boltzmann constant and

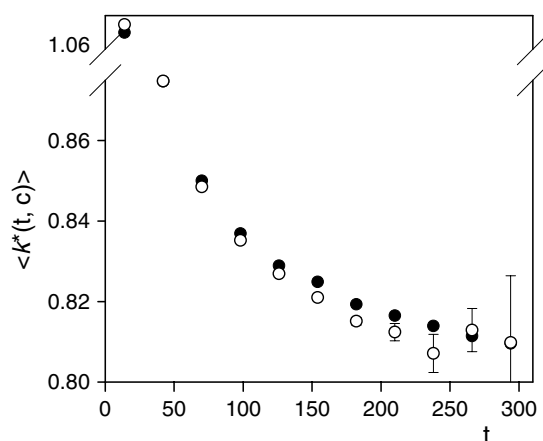
$$\mathbf{v}_i(t) = (\mathbf{v}_i(t + \delta t/2) + \mathbf{v}_i(t - \delta t/2))/2.$$

Both for the classical and the Brownian systems the time step  $\delta t$  was equal to  $0.01\sigma(m/\varepsilon)^{1/2}$ .

During the chemical process considered 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 relabelling A to C according to (2.2) and the condition was checked once per time step.

Two kinds of test have been performed for selected values of simulation parameters for all kinds of simulated system. The influence of the length of  $\delta t$  was tested by comparing the results with additional simulations for  $\delta t = 0.005\sigma(m/\varepsilon)^{1/2}$ . No significant difference between the results for different  $\delta t$  have been found. The randomness of the initial distribution of reagents was checked by performing additional simulations in which B components were assigned to the particles well before the moment that the reaction started. The fact that A and B diffused in space for a long time before the reaction started did not have any influence on the results obtained.

In first simulations of the QCDE [18] the inaccuracy of ‘measurements’ appeared to be a very serious problem. One of the ways applied here to improve the efficiency of computations was the adequate choice of  $u(r)$  (see (3.1)); another was the optimization of the computer program and the application of a method more suitable for the considered reaction model. The computer program has been modified as to perform many reaction runs going on at the same time during a single simulation run. Each reaction started at different  $t_{\text{run}}$  and went for the total reaction time,  $t_T$ . The ‘distance’ between subsequent  $t_{\text{run}}$  was always so high that the reaction runs could be treated as independent ones. The technique described above has been combined with the method of prerecorded trajectory [19–21], which benefits from the fact that the reaction (2.1) does not disturb the physical evolution of the system. The method considers a chemical system built up of  $L^3$  subsystems obtained by translating positions of the particles of the basic  $N$ -particle system  $L$  times in each of three ( $x$ ,  $y$ ,  $z$ ) directions. The ‘physical part’ of time evolution is realized by repeating the evolution of the basic system in each of the subsystems. But the chemical process 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 being 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 it significantly decreases the scale of the possible inconsistency between the results for different numbers of reagents (the size effect). It has been shown that for  $L = 1$  an inconsistency may appear when the number fraction of A reaches a very low value [21]. The above procedure was applied for all the simulations presented here. The simulations were carried out for  $N = 216\,000$ – $2299\,986$  and  $L = 3$ – $7$ . The largest system corresponded to nearly  $10^9$  reagents ( $2299\,986 \times 343$  for the liquid of number density  $\rho = 0.72$ ). For each of the simulation points (given  $\rho$ ,  $T$ ,  $c$ ) series



**Figure 1.** The reduced averaged rate coefficient,  $\langle k^*(t, c) \rangle = \langle k(t, c) \rangle_{\Delta t} / (4\pi Da)$  (from (2.5)), for the low-density liquid for  $a = \sigma$ . Empty circles,  $c = 0.0144$ ; filled circles,  $c = 5.86 \times 10^{-5}$ . The averaging of  $k(t, c)$  has been performed over the time intervals of the length of 28.0. All values are in reduced units. The error bars give the standard deviation.

of independent reaction runs (each for different  $t_{\text{run}}$ ) were performed. The number of runs was never lower than four. This enabled us to estimate the error for each of the simulation point by evaluating the standard deviation for the series [21]. More information on the optimization and other simulation details can be found in [21–23].

Six different systems each for a few values of  $c$  were simulated: a gas (number density  $\rho = 0.0288$ , mutual diffusion constant  $D = 17.4$ ), a low-density liquid ( $\rho = 0.72$ ,  $D = 0.316$ ), a high-density liquid ( $\rho = 1.04$ ,  $D = 0.045$ ), and three Brownian systems (BR1:  $\rho = 0.0072$ ,  $D_B = 0.370$ ; BR2:  $\rho = 0.0288$ ,  $D_B = 0.158$ ; BR3:  $\rho = 0.0208$ ,  $D_B = 0.0225$ ). The reduced temperature,  $k_B T / \varepsilon$ , was always 1.25. Here, the mutual diffusion constant  $D$  is equal to double the value of the self-diffusion constant for a simple fluid (physically all the particles are identical). The values of  $D$  were obtained directly from simulations by using the Einstein formula [25]. The values of  $D_B$  (see (3.2)) for BR2 and BR3 have been chosen to be equal to  $D/2$  for the low-density and the high-density liquid respectively.

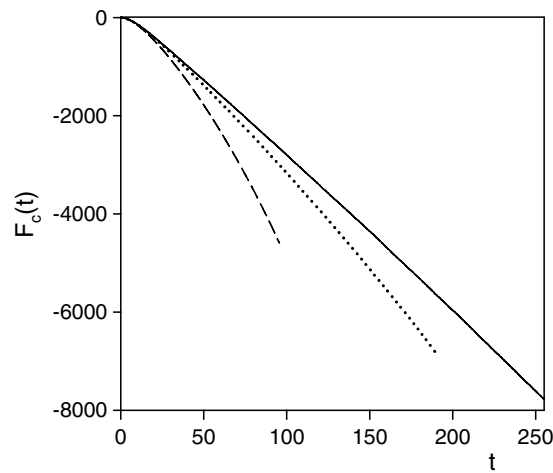
## 4. Simulation results and discussion

### 4.1. General results

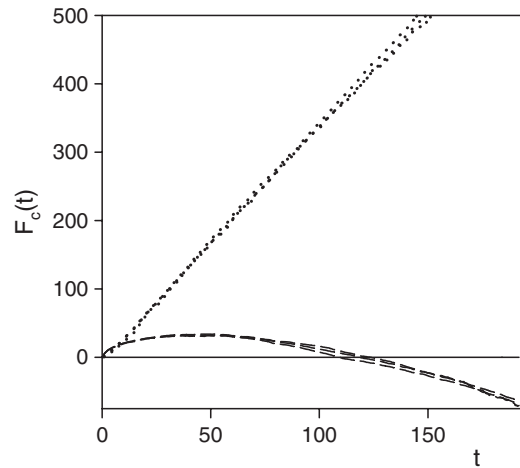
One of the results of the simulations is that both for the liquids and the gas considered the excess in the reaction rate is negative in the long-time limit [21, 23]. As an example, figure 1 presents  $\langle k(t, c) \rangle_{\Delta t}$  for the low-density liquid for two values of  $c$ . Considering estimated errors, it is clearly seen that, for high  $t$ , the values of  $\langle k(t, c) \rangle_{\Delta t}$  for higher  $c$  (empty circles) are significantly lower than the values for lower  $c$  (filled circles).

The decrease in  $k(t, c)$  with increasing  $c$  at long times can be also obtained applying (2.9) to the  $F_C$  curves presented in figure 2 (the gas).

Analysing figure 1, one can note that for short times  $\langle k(t, c) \rangle_{\Delta t}$  for higher  $c$  is higher than that for lower concentration. The effect is not a result of random deviation.  $\Delta k$  for liquids at short times is positive. Figure 3 shows the time evolutions of  $F_c$  for three concentrations of B



**Figure 2.**  $F_c(t)$  (from (2.10)) for the reaction in the gas for  $a = \sigma$ . The solid line,  $c = 0.0036$ ; the dotted line,  $c = 0.0072$ ; the dashed line,  $c = 0.0144$ . Application of (2.9) to the  $F_c(t)$  curves shows that after a quite short time  $\Delta k/c$  reaches a constant value which is a function of  $c$ .



**Figure 3.**  $F_c(t)$  for different systems. The dashed line: the low-density liquid for  $a = \sigma$  ( $D = 0.316$ ). The dotted line: the Brownian system BR2 for  $a = \sigma$  ( $D_B = 0.158$ ). Different curves within the same denotation represent different concentrations of B:  $c = 0.0036, 0.0072, 0.0144$ .

for the low-density liquid (the dashed lines) and for the Brownian system BR2 (the dotted lines). Considering relation (2.9), the figure illustrates two very surprising results of the simulations.

- (1) Both for the low- and the high-density liquid the excess in the rate coefficient was positive at short times [21]. The excess became negative for large  $t$ . The range of the region for which  $F_c(t) > 0$  depended on  $\rho$  and  $a$  [23]. The region was very small (or even absent) for the gas and, in general, increased with  $\rho$ .
- (2) For all the Brownian systems, the excess in  $k(t, c)$  was positive and constant, except for very short times. This property was checked for the range of times a few times larger than

in figure 3. In some cases the concentration of A changed by over four orders in magnitude during the test but any significant deviation from the rule was not observed [22].

The  $F_c(t)$  curves from figure 3 look to be independent of  $c$ . Some results suggests that, especially for the Brownian systems, the universality more exactly concerns  $\Delta k/c$  than  $F_c(t)$  (see the discussion on figures 3 and 5 in [22]). But, as is evident from figure 2, the universality does not hold for the gas. A more precise analysis of the curves from figure 2 shows that for the gas,  $\Delta k/c$  also depends on  $c$  (see also [23]). The scale of the excess for the gas system is many times larger than for the Brownian one as well as for the liquid (see figures 2 and 3; note that the values of  $c$  for the three systems are the same). Probably, the universality holds only if the scale of the process is sufficiently low, which is a consequence of the fact that (2.8) corresponds to the density expansion [24] truncated to  $O(c^2)$ .

One of the reasons of this strange behaviour of the Brownian systems may be the influence of A–A and A–C interactions on the rate of the reaction (2.1). To explain this qualitatively, first note that due to interparticle interactions,  $D$  for the Brownian system is not equal to but is slightly lower than  $2D_B$  (see [22]). In the limit  $c \rightarrow \rho$  the mutual diffusion constant for the reaction is equal to  $D/2 + D_B$  since A can collide only with B, which leads to the reaction. On the other hand, for  $c \rightarrow 0$  the constant for the process is  $D$  since A collides infinitely many times before (2.1) is realized. Therefore, the mutual diffusion constant for the reaction increases with increasing  $c$ , which means that the described mechanism gives a positive contribution to  $\Delta k$ . A deeper analysis and a simple model for the effect (which qualitatively agrees with the simulation results) are presented in [22].

Szabo has shown [2] that the steady state rate constant for the case of infinitely slow recombination ( $k_{SS}$ ) can be evaluated by integrating  $S(t, c)$  over time. The results of the long-time evolutions for liquids [21] have been used to evaluate  $k_{SS}$  and, as a result, the excess values ( $\Delta k_{SS}$ ) for a wide range of  $c$ . This enabled a comparison of the simulation results with the theoretical predictions for  $k_{SS}$  of Felderhof and Deutch [9] and Tokuyama and Cukier [10]. Using Szabo's formula for  $k_{SS}$  for the Smoluchowski model [2] one can show [21] that both theoretical predictions give the formula for  $\Delta k_{SS}$  which in the lowest order in  $\phi (= 4\pi a^3/3)$  can be written as

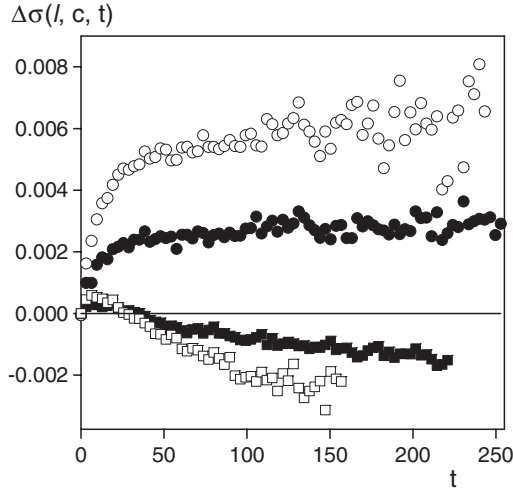
$$\Delta k_{SS}/(4\pi Da) = (3/2)\phi \ln \phi + (b_0 + 6/\pi - 3)\phi + \dots \quad (4.1)$$

where  $b_0$  is a constant that slightly depends on the model.  $\Delta k_{SS}$  predicted by (4.1) changes sign from positive for high  $c$  to negative for  $c \rightarrow 0$ . This agrees with the simulations for liquids. The fact that for high  $c$  the excess in  $k_{SS}$  is positive is a direct consequence of the presence of a time interval in which  $F_C > 0$  (see figure 3 and [21]). But quantitative differences between (4.1) and the simulations are very high. The simulation values are over an order of magnitude lower than the predictions and the value of  $c$  for which according to (4.1)  $\Delta k_{SS} = 0$  is about two orders of magnitude lower than that obtained from simulations [21]. The excess in  $k_{SS}$  is proportional to the integral of  $\Delta S(t, c)$ . Figure 3 shows that according to (2.8) the integral for the Brownian system, and as a consequence the excess value, is positive and much higher than that for the considered liquid. This is closer to the prediction of (4.1) for high  $c$  than that for the liquids. But on the other hand, the results obtained have not shown any tendency for  $\Delta S(t, c)$  for the Brownian systems to change sign with decreasing  $c$ , which disagrees with (4.1) that predicts negative value for  $c \rightarrow 0$ .

#### 4.2. Correlation with the spatial correlations [22]

The simulations for the deterministic liquids and the Brownian systems have shown a strong correlation between  $\Delta k$  and the excess in the relative spatial correlations between A and B





**Figure 4.** The excess in the relative spatial correlation,  $\Delta\sigma_{AB}(l, c, t)$  (from (4.3)), as a function of  $t$ . The circles: the Brownian system (as in figure 3,  $l = 4.95$ ; empty:  $c = 0.0144$ , filled:  $c = 0.0072$ ). The squares: the deterministic liquid (as in figure 3,  $l = 4.91$ ; empty:  $c = 0.0144$ , filled:  $c = 0.0072$ ).

defined as

$$\Delta\sigma_{AB}(l, c, t) = \sigma_{AB}(l, c, t) - \sigma_{AB}(l, c_0, t) \quad (4.2)$$

where

$$\sigma_{AB}(l, c, t) = \frac{\langle n_A(t)n_B(t) \rangle_l}{\langle n_A(t) \rangle_l \langle n_B(t) \rangle_l} - 1. \quad (4.3)$$

$n_X(t)$  is current number of the X particles enclosed in an imaginary cell of box-length  $l$ ,  $\langle \rangle_l$  is the spatial average over the cell, and  $c_0$  is sufficiently low to make the definition (4.2) reasonable.

The values of  $\Delta\sigma_{AB}(l, c, t)$  as a function of  $t$  for the Brownian system (the circles) and for the deterministic liquid (the squares) are presented in figure 4. The data presented in figures 3 and 4 come from the same simulation runs (except for  $c = 0.0036$ , which is absent in figure 4). The correlation between  $\partial F_c / \partial t (\cong \Delta k / c)$  and  $\Delta\sigma_{AB}(l, c, t) / c$  is evident. The only small inconsistency is that the time when  $\Delta\sigma_{AB}(l, c, t) = 0$  for the deterministic system does not match exactly with that of the maximum of  $F_c(t)$  in figure 3.

#### 4.3. Analysis via the two-particle probability density function [23]

It seems obvious that positive or negative values of  $\Delta\sigma_{AB}(l, c, t)$  result in an increase or a decrease (respectively) of the rate of the reaction (2.1). But very recent simulations have shown that for the gas  $\Delta\sigma_{AB}(l, c, t)$  is positive in spite of  $\partial F_c / \partial t$  is negative (as in figure 2). This completely disagrees with the results for the liquid and the Brownian systems discussed in section 4.2. The reason is that, strictly speaking, the excess in the reaction rate is not a consequence of  $\Delta\sigma_{AB}(l, c, t)$  itself but it is a direct consequence of the excess in the flux of A towards B at  $r = a$ . The flux can be written as a product of  $G_{AB}(r, t)$  (the probability density function for AB pairs,  $f_{AB}(\mathbf{r}, \mathbf{v}, t)$ , integrated over the relative velocity,  $\mathbf{v}$ ) and  $U_{AB}(r, t)$  (the mean value of the radial velocity of A towards B, i.e. the first radial moment). Therefore we

can write

$$\Delta k(t, c)/k(t, c) = \Delta G(a, t)/G(a, t) + \Delta U(a, t)/U(a, t) \quad (4.4)$$

where  $\Delta X$  means the excess in  $X$  and the term  $\Delta G \Delta U$  has been neglected.

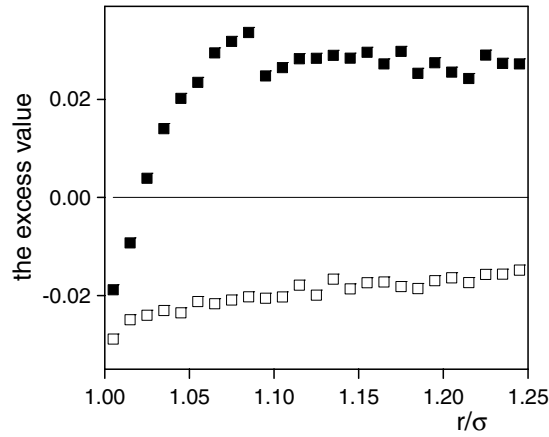
$G_{AB}(r, t)$ ,  $U_{AB}(r, t)$ , and the second radial moment of  $f_{AB}(\mathbf{r}, \mathbf{v}, t)$ , denoted as  $UU_{AB}(r, t)$ , were ‘measured’ directly during the simulations. The data from a given time  $t_0$  to the total time of the reaction  $t_T$  were used to evaluate the time averages (denoted as  $\langle X \rangle$  where  $X$  is the value). The value of  $t_0$  was chosen to be high so as to obtain a time average that may be treated as an asymptotic one. For the gas and the Brownian system, the procedure worked quite well and the obtained averages should be close to the real asymptotic values. The analysis of the  $F_C$  curves from figures 2 and 3 show that, for these systems,  $\Delta k$  becomes approximately constant after a reasonably short time. But for the liquid no tendency for  $\Delta k$  to attain a constant value is noted (figures 1 and 3), which shows that the collected data do not represent the asymptotic state. In this case  $t_0$  were chosen to be well above the time when  $\Delta k = 0$ . The obtained time averages can be only treated as very rough approximations for the asymptotic values; however, it seems very reasonable to assume the properties of the values to be very close to that for  $t \rightarrow \infty$ .

Averaging (4.4) over long times and neglecting the correlations between  $\langle \Delta X \rangle$  and  $\langle X \rangle$ , one obtains (4.4) with  $k$ ,  $G$ ,  $U$ , and the excess values replaced by the time averages. Equation (4.4) in the averaged form has been used to analyse the influence of  $\Delta U_{AB}(a, t)$  and  $\Delta G_{AB}(a, t)$  on the excess in  $k(t, c)$ . The most important results were as follows.

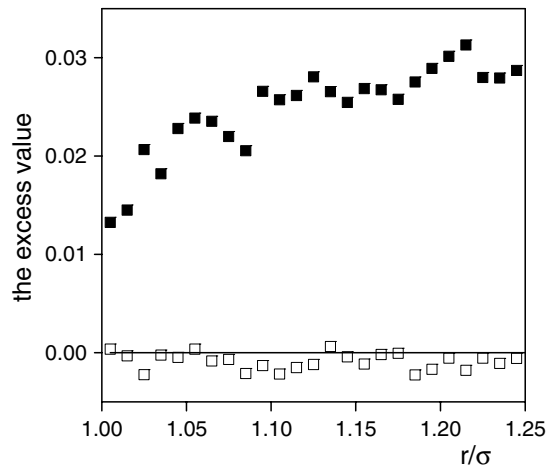
- (1) For the gas, the contribution to  $\Delta k$  from  $\langle \Delta U_{AB}(a, t) \rangle / \langle U_{AB}(a, t) \rangle$  was negative and it dominated over that from  $\langle \Delta G_{AB}(a, t) \rangle / \langle G_{AB}(a, t) \rangle$ . As a result,  $\Delta k$  for the gas was always negative in spite of  $\langle \Delta G_{AB}(a, t) \rangle / \langle G_{AB}(a, t) \rangle$  which was negative for  $a = \sigma$  and positive for  $a = 1.08\sigma$ ;
- (2) For the Brownian system,  $\langle \Delta U_{AB}(a, t) \rangle / \langle U_{AB}(a, t) \rangle$  was equal to 0 (to the accuracy of the measurements) and  $\Delta k$  resulted only from  $\langle \Delta G_{AB}(a, t) \rangle / \langle G_{AB}(a, t) \rangle$  which was positive.
- (3) For the low-density liquid,  $\langle \Delta U_{AB}(a, t) \rangle / \langle U_{AB}(a, t) \rangle$  depended on  $a$ . It was negligible if  $a = 1.08\sigma$  (the activation energy = 0) and became significant (and negative) if  $a = \sigma$ . For the high-density liquid ( $a = \sigma$ , the only case considered),  $\langle \Delta U_{AB}(a, t) \rangle / \langle U_{AB}(a, t) \rangle$  was 0.  $\langle \Delta G_{AB}(a, t) \rangle / \langle G_{AB}(a, t) \rangle$  was negative for all the liquids considered.
- (4) The excess in  $\langle UU_{AB}(r, t) \rangle - \langle U_{AB}(r, t) \rangle^2$  was noticeably only for the gas.

The cases (1) and (2) are illustrated in figures 5 and 6 that present  $\langle \Delta U_{AB}(r, t) \rangle / \langle U_{AB}(a, t) \rangle$  and  $\langle \Delta G_{AB}(r, t) \rangle / \langle G_{AB}(a, t) \rangle$  for the gas and for the Brownian system BR2 (both for  $a = \sigma$ ) respectively. As is seen in figure 5, the absolute value of  $\langle \Delta U_{AB}(a, t) \rangle / \langle U_{AB}(a, t) \rangle$  is significantly higher than that of  $\langle \Delta G_{AB}(a, t) \rangle / \langle G_{AB}(a, t) \rangle$ . This was fulfilled also for  $a = 1.08\sigma$ ; however, in this case  $\langle \Delta G_{AB}(r, t) \rangle / \langle G_{AB}(a, t) \rangle$  was positive for all  $r$ . The fact that  $\langle \Delta G_{AB}(r, t) \rangle$  in figure 5 changes sign while approaching  $r = a$  is probably a result of the non-zero activation energy. The effect does not influence  $\langle \Delta G_{AB}(r, t) \rangle$  for the Brownian system (figure 6), which is positive for all  $r$ . The curves for the Brownian system for  $a = 1.08\sigma$  were qualitatively very similar to that from figure 6. Note that  $\langle \Delta U_{AB}(r, t) \rangle / \langle U_{AB}(a, t) \rangle$  in figure 6 is completely negligible when compared to  $\langle \Delta G_{AB}(r, t) \rangle / \langle G_{AB}(a, t) \rangle$ .

Both for the gas and for the Brownian system  $\langle \Delta G_{AB}(r, t) \rangle$  as a function of  $r$  is always (figure 6) or almost always (figure 5) positive, which results in a positive value of  $\Delta \sigma_{AB}(l, c, t)$  since the latter comes from the integration of  $\Delta G_{AB}(r, t)$ . The only significant qualitative difference between  $\langle \Delta G_{AB}(r, t) \rangle$  for the Brownian system and for the gas is that for the latter; but only for  $a = \sigma$  does  $\langle \Delta G_{AB}(r, t) \rangle$  change sign very close to  $r = a$ . This suggests the presence of a relation between the positive values of  $\langle \Delta G_{AB}(r, t) \rangle$  (and, as a result, positive  $\Delta k$  for the Brownian systems) and a low value of density, here equal to 0.0288 both for the



**Figure 5.**  $\langle \Delta U_{AB}(r, t) \rangle / \langle U_{AB}(a, t) \rangle$  (empty squares) and  $\langle \Delta G_{AB}(r, t) \rangle / \langle G_{AB}(a, t) \rangle$  (filled squares) for the gas,  $a = \sigma$  and  $c = 0.0072$ .



**Figure 6.** As in figure 5 but for the Brownian system BR2,  $a = \sigma$ .

gas and for the Brownian system. For the liquids ( $\rho = 0.72$  and  $1.04$ ) in the long-time limit,  $\langle \Delta G_{AB}(r, t) \rangle$  was negative for a wide range of  $r$ .

Negligibility of  $\Delta U_{AB}(r, t)$  both for the dense liquid and for the Brownian system (as in figure 6) suggests that the mechanism that leads to the QCDE depends on the relaxation time. If the relaxation is sufficiently fast,  $f_{AB}(\mathbf{r}, \mathbf{v}, t)$  depends on  $c$  only via a scaling factor. If it is slow,  $f_{AB}(\mathbf{r}, \mathbf{v}, t)$  deforms much more and the excesses in both  $U_{AB}(a, t)$  and  $U U_{AB}(a, t) - U_{AB}(a, t)^2$  are significant. From this point of view the low-density liquid belongs to a transition region.

The accuracy of ‘measurements’ for the high-density liquid was sufficient to estimate not only the long-time averages of  $\Delta U_{AB}(a, t)$  and  $\Delta G_{AB}(a, t)$  but also the time evolutions (averaging over short time intervals) for nearly all range of time ( $t > 4.0$ ). The result was that  $\Delta U_{AB}(a, t)$  was approximately zero for all times. The positive excess in  $k(t, c)$  that appeared for short times (see figure 3) was only a result of the positive excess in  $G_{AB}(a, t)$ . Therefore,

the strange region of positive excess in  $k(t, c)$  for liquids is not a result of a process similar to that for the gas.

## 5. Summary

Recent results of molecular dynamics simulation on the influence of the quencher concentration on the rate of the reaction (2.1) have been presented. The simulations clearly show that for long times  $\Delta k$  both for liquids and for gases is negative. But the reasons for the effect are not only simply fluctuations in concentrations of reagents. For the gas, the contribution to the excess in the rate coefficient coming from  $\Delta U_{AB}(a, t)$  is more important than that from  $\Delta G_{AB}(a, t)$ . The excess in  $U_{AB}(r, t)$  becomes 0 both for the dense liquid and for the Brownian system, which strongly suggests that the reason for the change in the mechanism that results in the QCDE is a drastic increase in the relaxation rate of  $f_{AB}(\mathbf{r}, \mathbf{v}, t)$  when compared to that for the gas.

One of the most important and surprising results of the simulations is that for a quite long time for liquids as well as for the whole range for the Brownian systems  $\Delta k$  and  $\Delta\sigma_{AB}(l, c, t)$  are positive. The positive excesses in  $\sigma_{AB}(l, c, t)$  and in  $G_{AB}(a, t)$  for the Brownian system are probably in some relation with the low value of  $\rho$  but the real nature of the effect is not known. A comment that may be useful in further investigations comes directly from the formulae for  $\Delta\sigma_{AB}(l, c, t)$  ((4.2) and (4.3)).  $\sigma_{AB}(l, c, t)$  is the relative value and, in general, it does not vanish for  $c \rightarrow 0$ . As a result, however, the fluctuations always lead to a decrease in the rate coefficient, but this does not mean that  $\Delta k$  (which is a result of subtraction) is negative. This is obviously also true for  $\Delta G_{AB}(a, t)$  and  $\Delta U_{AB}(a, t)$ .

One should also mention the fact which differs both real situation and computer simulations from standard theoretical approaches. In order to evaluate an excess value for a more or less realistic situation the systems compared must be physically identical. As a result, the total number of particles per unit volume must be conserved during the reaction as well, as it cannot change with changing  $c$ . As a consequence, the A–A and A–C interactions may significantly influence the investigated effect. A discussion and a very simple model for the influence are presented in [22] but the problem is worth more attention.

## References

- [1] Smoluchowski M 1917 *Z. Phys. Chem.* **92** 129
- [2] Szabo A 1989 *J. Phys. Chem.* **93** 6929
- [3] Lee S and Karplus M 1987 *J. Chem. Phys.* **86** 1883
- [4] Felderhof B U and Jones R B 1995 *J. Chem. Phys.* **103** 10201
- [5] Yang M, Lee S and Shin K J 1998 *J. Chem. Phys.* **108** 117
- [6] Yang M, Lee S and Shin K J 1998 *J. Chem. Phys.* **108** 8557
- [7] Gopich I V, Kipriyanov A A and Doktorov A B 1999 *J. Chem. Phys.* **110** 10888
- [8] Sung J and Lee S 1999 *J. Chem. Phys.* **111** 10159
- [9] Felderhof B U and Deutch J M 1976 *J. Chem. Phys.* **64** 4551
- [10] Tokuyama M and Cukier R I 1982 *J. Chem. Phys.* **76** 6202
- [11] Gopich I V, Berezhovskii A M and Szabo A 2002 *J. Chem. Phys.* **117** 2987
- [12] Blumen A, Zumofen G and Klafter J 1984 *Phys. Rev. B* **30** 5379
- [13] Bramson M and Lebovitz J L 1988 *Phys. Rev. Lett.* **61** 2397
- [14] Bramson M and Lebovitz J L 1991 *J. Stat. Phys.* **62** 297
- [15] Oshanin G, Benichou O, Coppey M and Moreau M 2002 *Phys. Rev. E* **66** 060101
- [16] Zhou H-X and Szabo A 1991 *J. Chem. Phys.* **95** 5948
- [17] Senapati S, Wong C F and McCammon J A 2004 *J. Chem. Phys.* **121** 7896
- [18] Litniewski M and Gorecki J 2005 *J. Chem. Phys.* **122** 204504
- [19] Gorecki J 1995 *Mol. Phys. Rep.* **10** 157
- [20] Nowakowski B, Kawczynski A and Gorecki J 1999 *J. Phys. Chem. A* **103** 3200

- [21] Litniewski M 2005 *J. Chem. Phys.* **123** 124506
- [22] Litniewski M 2006 *J. Chem. Phys.* **124** 114501
- [23] Litniewski M 2006 *J. Chem. Phys.* **125** 174501
- [24] Szabo A, Zwanzig R and Agmon N 1988 *Phys. Rev. Lett.* **61** 2496
- [25] Allen M P and Tildesley D J 1987 *Computer Simulations of Liquids* (Oxford: Oxford University)
- [26] Verlet L 1967 *Phys. Rev.* **159** 98
- [27] Kloden P E and Klaten E 1992 *Numerical Solutions of Stochastic Differential Equations* (Berlin: Springer)