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## Ab initio kinetic Monte Carlo simulation of seeded emulsion polymerizations of styrene

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Seeded emulsion polymerizations of styrene are modeled on the basis of a detailed kinetic scheme accounting for the chain length and conversion dependence of termination rate coefficients. A holistic kinetic Monte Carlo approach was developed, which simulates the elemental reactions in the aqueous phase, the transfer of radicals into individual particles, and the radical polymerization in each particle based on a complete kinetic model. Experimentally-derived particle size distributions are used as input for the simulations. The required rate coefficients were taken from literature. Without any adjustment of this data a very good agreement between simulation results and experimental data is found. The validation of the model is performed based on monomer conversion – time data and full molar mass distributions.

### Introduction

Emulsion polymerization processes are associated with a number of advantages, such as excellent heat dissipation, low viscosity of the emulsion, and a high weight fraction of polymer in the latex. Since water is used as the continuous phase in most cases the processes are considered to be environmentally friendly. Due to the compartmentalization of radicals into particles, higher polymerization rates and molar masses are achieved compared to polymerizations in bulk or solution.<sup>1</sup> The latex produced has many applications. For example it may be used directly as surface coating or after processing as bulk polymer.<sup>2,3</sup>

The kinetics of emulsion polymerizations are complex. In addition to the common elemental reaction steps in radical polymerization (initiation, propagation, transfer and termination), it is necessary to consider radical phase-transfer processes.<sup>4</sup> The reaction starts in the aqueous phase. Then, the radical formed passes through a few propagation steps in the continuous phase before it enters a particle. Apart from this so-called radical entry process, a radical can also leave a particle (radical exit). Polymerization takes exclusively place in the particles. Each particle can be considered as a nanoreactor. In addition to radical entry and exit, the key mechanistic aspects include particle formation and growth, as well as termination processes and secondary nucleation.<sup>2</sup> Reliable modelling of emulsion polymerizations has to consider all these processes.

For a typical batch emulsion polymerization three distinct intervals are operative.<sup>5</sup> In interval I particle formation takes place.

Monomer droplets, surfactant molecules, micelles in cases of surfactant concentrations being above the critical micelle concentration, and precursor particles are present. Interval II is characterized by a constant particle number. The particles grow by propagation in the presences of monomer droplets, which serve as a reservoir for monomer ensuring that the monomer concentration in the particles is constant. In interval III no monomer droplets are present and particle growth can be neglected. The remaining monomer in the particles is polymerized.<sup>2,3</sup>

To gain a deeper understanding of mechanistic aspects related to emulsion polymerizations experimental data was modeled. Frequently, the emulsion polymerization of styrene<sup>6</sup> was considered. Thus, this system often serves as a reference. For radical entry the most widely accepted model is the propagation-controlled mechanism.<sup>7</sup> This model, introduced by Maxwell *et al.*,<sup>8</sup> assumes that a radical grows in the aqueous phase up to a critical chain length until it becomes surface active and then enters a particle. Another important aspect of the emulsion polymerization is reduced termination due to compartmentalization of radicals. Therefore, two approaches were put forward, the zero-one and the pseudo-bulk model.<sup>9</sup> In the zero-one model particles with two or more radicals are neglected. It is assumed, that termination is pseudo instantaneous. Typically, this approach is applied to simulate the polymerization in small particles at low conversion. It also allows for checking, if a system obeys zero-one kinetics. The group of Gilbert applied this model to interpret the mechanism of particle formation.<sup>1,10</sup> The pseudo-bulk approach assumes that all particles of the same size have the same average number of radicals. Systems with a high number of radicals per particle or high radical entry rates are described well by this model. Compared to the zero-one approach, it allows for the simulation of the emulsion

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discussed above radical exit can be neglected due to the high viscosity inside the particles. Because of the simplifications associated with the selected polymerization conditions, the method of seeding is of particular interest to study the mechanism of emulsion polymerization and to establish new holistic modeling approaches.<sup>3</sup>

The polymerization in the particles is assumed to be well treated as a bulk polymerization. Due to the excellent knowledge of styrene bulk polymerization kinetics, this system provides a reliable basis to verify the current modeling approach. In addition to the propagation rate coefficient,  $k_p$ ,<sup>35</sup> and the transfer rate coefficient to monomer,  $k_{tm}$ ,<sup>36</sup> the termination rate coefficients,  $k_t$ , have been extensively studied. Buback and Kattner introduced a composite model accounting for the chain-length dependence of  $k_t$ <sup>37</sup> and an extension for polymerizations up to high conversions.<sup>38</sup>

The modeling approach presented for the seeded emulsion polymerization of styrene aims to demonstrate the feasibility of simulating experimental data without the need of adjusting any coefficients. The polymerization is performed in a large ensemble of discrete pre-synthesized polymer particles with different sizes, thus, the compartmentalization of radicals is naturally taken into account. Therefore, it is possible to model the process without further assumptions with respect to the termination kinetics in contrast to approaches published, where termination rate coefficients were manipulated to simulate the separation of radicals inside the particles. The aqueous phase is also simulated by the kMC approach to generate the radicals, which will be transferred into the particles. The combination of the simulation of aqueous phase and the simulation in the particles results in a holistic model that describes the experimental reality as accurately as possible.

## Experimental

### Materials

The surfactant Aerosol MA 80 (technical grade ~80% in H<sub>2</sub>O, Sigma-Aldrich), the initiator potassium persulfate (KPS, >98%, MERCK) and sodium hydrogen carbonate ( $\geq 99\%$ , Roth) were used as received. The inhibitor was removed from styrene (99.5%, Sigma-Aldrich) by distillation under reduced pressure. Tetrahydrofuran (THF, 99%, VWR Prolab) was distilled prior to use as eluent for size-exclusion chromatography.

### Preparation of the polystyrene seed

Typically, 3.2 g (0.04 mol L<sup>-1</sup>) of the surfactant Aerosol MA80 and 0.2 g (0.012 mol L<sup>-1</sup>) of sodium hydrogen carbonate, which was used as buffer, were dissolved in 165 g Milli-Q (Millipore) deionized water. The solution was heated up to 70 °C in a 250 mL double-jacketed stainless steel reactor under stirring with an impeller agitator at 500 rpm. During the heat-up phase the reactor was purged with nitrogen. After the reaction temperature was reached, 32 g of styrene and 0.16 g ( $3 \times 10^{-3}$  mol L<sup>-1</sup>) of potassium persulfate were added. After a polymerization time of two hours the reaction mixture was heated to 85 °C to remove residual KPS. The recipe was adapted from the work of

Winschel.<sup>39</sup> For one reaction the stirrer speed was reduced to 345 rpm.

### Seeded emulsion polymerization

The seeded emulsion polymerization was usually carried out as follows. 70 g of polystyrene seed produced in the first step was mixed with 60 g of deionized water and 0.06 g ( $5 \times 10^{-3}$  mol L<sup>-1</sup>) of sodium hydrogen carbonate. After the reaction mixture was heated to 70 °C 11.2 g of styrene was added. In one case 7.3 g of styrene were used at otherwise identical conditions. To achieve an almost complete swelling of the particles with the monomer, the solution was stirred at 550 rpm for five hours under nitrogen and subsequently 0.07 g ( $1.8 \times 10^{-3}$  mol L<sup>-1</sup>) of KPS was added. The reaction was terminated after two hours. The conversion was measured gravimetrically by weighing the dry content of the samples.

### Size-exclusion chromatography

Molar mass distributions were determined by size-exclusion chromatography using a Waters 515 HPLC pump, a Knauer Marathon autosampler, a Knauer Smartline refractive index Detector 2300, and four PSS SDV columns (guard, 100 Å, 1000 Å and 100 000 Å). The system is operated at 25 °C and THF is used as eluent with a flow rate of 1 mL min<sup>-1</sup>. Calibration was established with narrow polystyrene standards (PSS) with number average molar masses,  $M_n$ , ranging from 700 to  $2.57 \times 10^6$  g mol<sup>-1</sup>.

### Dynamic light scattering

Dynamic light scattering (DLS) measurements were carried out using an instrument from ALV (Langen, Germany) at 25 °C. For the discussion of the experimental results mass-weighted radii were considered.

### Computing resources

The simulations were executed on application servers (transtec CALLEO, 2xIntel Xeon E5-2670 CPU 16 cores, 2.6 GHz, 256 GB RAM) running a virtualized CentOS 7.3 Linux operating system. Compilation of the simulation program written in C++ was executed with gcc 4.8.5. In addition, the Open MPI v2.1.1 software environment<sup>40</sup> was integrated for the parallelization of the simulation.

### Modeling strategy

The model introduced for the seeded emulsion polymerization of styrene links the kinetic Monte Carlo simulation of a radical polymerization with the special requirements for an emulsion polymerization: radical generation and propagation in the aqueous phase, transfer of radicals into the particles and polymerization in isolated particles. Contrary to other modeling approaches, in this work the particles are of realistic size. Thus, each particle contains a discrete number of monomer molecules that correlates with the particle size. During polymerization each particle constitutes a polymerization reactor with a real volume, which is associated with the complete kinetic polymerization model consisting of chain propagation, transfer to monomer, and bimolecular termination.







inside the particles at defined time stamps. Furthermore, the master process takes care of the aqueous phase model, in particular with respect to the generation of macroradicals triggering the polymerization in the particles.

On the right hand side of Fig. 4 the slaves handle simulation instances of individual particles. Here, typically 4000 to 8000 particles were assigned to each slave with 16 slave processes in total. During the initialization phase the master process prepared parameters for each particle, which serve as input in the kMC simulation set-up. Particles are assumed to be discrete reactors simulated by an instance of the mcPolymer simulation program.<sup>33</sup> After the initialization all particles remain non-reactive due to the lack of macroradicals inside.

At a distinct point in time  $t_1, t_2, \dots$  macroradicals of type  $R_2$  will be generated in the aqueous phase. The master process recognizes the presence of such a macroradical at time  $= t_x$  and will select one of the slaves as target for the radical entry in a particle. Per definition all slave processes have an equal probability for radical transfer. This is a valid approach due to the large number of stored particles in each slave representing the particle size distribution of the entire model. A second selection step takes place inside the slave process picking a distinct particle from its pool of particles according to a probability, which correlates with the surface area of a single particle.

The communication between the master and its slave processes is realized with the Message Passing Interface (MPI).<sup>49</sup> Each message contains a time stamp for the radical transfer and the chain length of the macroradical. Message transfer is a non-blocking operation; the master will not wait for an acknowledgement of the slave and will continue its simulation process (fire & forget policy).

Particle simulations run on their own timeline and will advance to the point in time  $t_x$  of every related macroradical entry. The kMC calculations in the particles are provided by the slave processes, which determine the calculation speed of the whole simulation. Those slave knots and their local simulation processes are only loosely coupled to the master and totally

independent of each other, thus, allowing to scale efficiently the simulation on many parallel processor cores making use of the resources of multi-processor systems. Thus, the architectural layout of the simulation approach is very close to the experimental reality.

## Results and discussion

### Experimental validation

Three styrene swollen seeds (SwS1, SwS2 and SwS3) differing in particle size and molar mass distribution were selected for experimental validation of the modeling approach described above. The seeds are characterized in Table 2. SwS1 and SwS2 are associated with the same mean radius, whereas the particles of SwS3 are slightly larger. Fig. 5 shows the same behavior for the corresponding DLS-derived particle size distributions. In addition, it is seen that the PSD for latex SP3 obtained after polymerization is shifted to larger values compared to the PSD of the initial seed SwS3. The mean radius is increased from 52 to 57 nm. The shape of the PSD is not varied significantly after polymerization. Since the probability of radical entry is calculated based on relative particle sizes the shift of the entire PSD does not affect modeling of the radical entry throughout the entire polymerization.

Seeded emulsion polymerization SP1 to SP3 were carried out with the same KPS concentration. In addition, reactions with increased (SP4) or reduced (SP5) initiator concentration were performed. The seeds used, the reaction time, and the styrene concentration inside the particle,  $c_s(\text{particle})$  are listed in Table 3. The experimental results may be used for analyzing

Table 2 Properties (number average molar mass ( $M_n$ ), weight average molar mass ( $M_w$ ), dispersity ( $D$ )) of the seeds used for the emulsion polymerization of styrene. The mean radius was determined after swelling the particles with monomer

Sample	Mean radius, nm	$M_n$ , kg mol <sup>-1</sup>	$M_w$ , kg mol <sup>-1</sup>	$D$
SwS1	43	84.0	633	7.5
SwS2	44	229	865	3.9
SwS3	52	58.3	225	3.9
SwS4	45	235	866	3.7

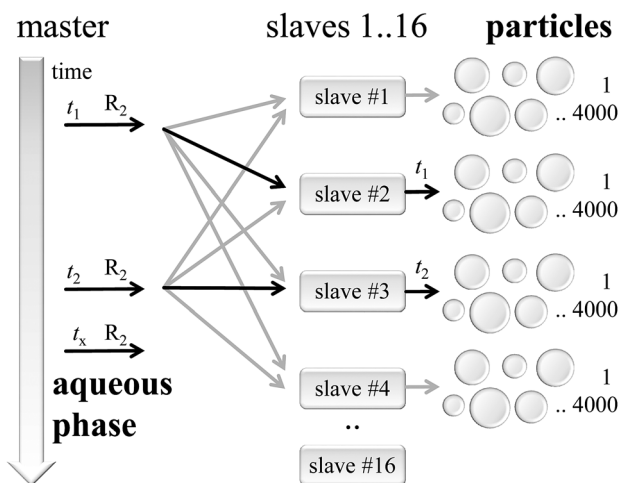


Fig. 4 Master-slave software architecture, connecting the aqueous phase with particles.

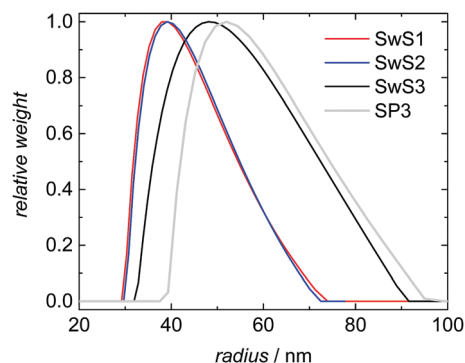


Fig. 5 DLS-derived particle size distributions for monomer swollen seeds SwS1 to SwS3 and for SP3 after polymerization starting with SwS3.





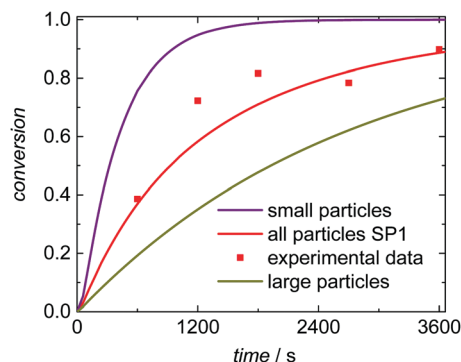


Fig. 7 Simulation results and experimental data of emulsion polymerization SP1. Conversion vs. time data is shown for the total ensemble of particles, for the fraction of small particles with radii between 64.0 and 68.5 nm, and for the fraction of large particles with radii ranging from 118 to 141 nm.

evaluated for (i) the entire ensemble of particles, (ii) the fraction of small particles with radii between 64.0 and 68.5 nm, (iii) and for the fraction of large particles with radii ranging from 118 to 141 nm. The absolute numbers of radicals inside a particle are expected to be rather close. Thus, for this special aspect a rather large ensemble consisting of 512 000 particles was simulated simultaneously to identify statistically sound contributions of the fractions of small and large particles on conversion and molar mass distributions. Within the first 600 s of polymerization time the number of radicals per small particles was 1.46 and 1.50 in case of the large particles. This argument may explain the differences in the conversion vs. time data in Fig. 7. The smaller the particles the faster the monomer conversion in a given time interval. These differences are paralleled with variations in the molar mass distributions due to differing termination rates. For comparison a monomer conversion of 0.50 is chosen. If the entire ensemble of particles is considered,  $M_n$  is  $716 \text{ kg mol}^{-1}$ . The fraction of small particles leads to polymer with  $M_n$  of  $805 \text{ kg mol}^{-1}$  and for the larger particles  $M_n$  is  $657 \text{ kg mol}^{-1}$ .

The simulated and experimentally determined conversion vs. time data for SP4 and SP5 given in Fig. 8 show a good agreement as well. Both experiments and simulations show

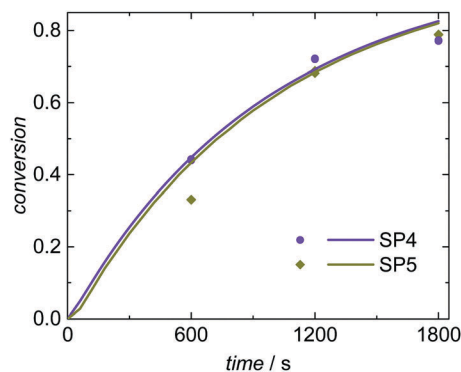


Fig. 8 Conversion vs. time data for seeded emulsion polymerization with increased (SP4) and decreased (SP5) initiator concentration. Polymerizations were carried out starting from the same seed (SwS4). The markers represent experimental data and the full lines modeling results.

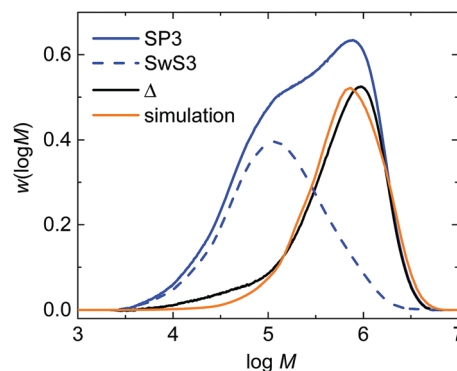


Fig. 9 Comparison of experimentally derived molar mass distributions and a simulated distribution. The label “ $\Delta$ ” refers to the curve obtained via subtraction of curve SP3 from SwS3. For further details the reader is referred to the main text.

very similar conversion vs. time data at high ( $3.5 \times 10^{-3} \text{ mol L}^{-1}$ ; SP4) and low ( $0.8 \times 10^{-3} \text{ mol L}^{-1}$ ; SP5) KPS concentrations. The evaluation of the radical balance in aqueous phase indicates an increase of the initiation efficiency  $f_{\text{entry}}$  with reduced KPS concentration. This trend is also described by Hawket *et al.*<sup>6</sup> For SP4 (high initiator concentration) an initiation efficiency of  $f_{\text{entry}} = 0.29$  is derived from the simulation. In comparison, for SP5 with decreased KPS concentration an initiation efficiency of  $f_{\text{entry}} = 0.46$  is determined. As discussed above, for a mean initiator concentration under otherwise similar conditions (SP1;  $c_{\text{KPS}} = 1.8 \times 10^{-3} \text{ mol L}^{-1}$ ) an intermediate value of 0.38 was obtained for  $f_{\text{entry}}$ . Due to these opposing variations in  $c_{\text{KPS}}$  and  $f_{\text{entry}}$  the radical flux is rather similar for SP1, SP4 and SP5. Consequently, there are just minor differences in the conversion vs. time data.

The experimental validation of the simulated molar mass distributions is depicted in Fig. 9 for experiment SP3. The figure shows the experimental distribution of the seed (SwS3) and the latex after the seeded emulsion polymerization (SP3). In addition, the simulated distribution is given. Since the seed was associated with a rather low  $M_n$  of  $53.8 \text{ kg mol}^{-1}$  and the product obtained during the seeded emulsion polymerization is of rather high  $M_n$  the molar mass distributions is bimodal, being indicative of both fractions of polymer. After the seeded emulsion polymerization is finalized the weight fraction of the seed inside the particle is 0.5. To obtain an estimate of the molar mass distribution (MMD) for the polymer of the seeded emulsion polymerization the MMD of the seed is multiplied with 0.5 and then subtracted from the MMD of SP3 resulting in the curve labeled with “ $\Delta$ ” in Fig. 9. The simulated MMD originates from modeling with an ensemble of 64 000 particles and a total number of  $4.519 \times 10^7$  discrete polymer chains. The comparison of the simulated MMD with the distribution labelled “ $\Delta$ ” shows a very good agreement. This result strongly supports the model approach chosen. It should be noted that all kinetic data is taken from literature. There are no adjustable parameters in the model.

### Simulation design

It goes without saying that the time required for computing increases with the number of particles. The data given in



Fig. 6–9 was obtained with an ensemble size of 64 000 particles. This number is feasible, since a polymerization time of 60 min required a computing time of 124 min. Moreover, the resulting data set was sufficiently large to analyze subsets of the data, as shown in Fig. 7.

In the kMC simulation concentrations are expressed by discrete molecules. Due to the particle size, it is possible to simulate the particles with realistic molecule numbers. The continuous aqueous phase is coupled with a given number of discrete particles in this simulation approach. The particle number determines the dimension of the kMC model in the aqueous phase. The initiation and termination processes in the aqueous phase result in an initiation efficiency  $f_{\text{entry}}$  of less than 1. This influences the radical balance of the seeded emulsion polymerization. The initiation efficiency is calculated from the balance of all propagation and termination reactions in the aqueous phase shown in Fig. 2. It is particularly important that the bimolecular termination in the kMC simulation is calculated with a statistically sound number of species R1. Using 64 000 particles, a quasi-stationary molecule number R1 of about 1000 is observed, which corresponds to a concentration of about  $5 \times 10^{-8} \text{ mol L}^{-1}$ . As a result, at least 10 000 particles should be used in the simulation.

The variation of computing time with the number of particles was evaluated systematically for experiment SP1 to show which sample sizes are feasible. The results are listed in Table 4 and plotted in Fig. 10. As already detailed in the section on software architecture the calculation of the kinetic model in aqueous phase and the distribution of the macroradicals is administered in the master process, while the associated slave processes perform the kMC simulations in the particles. The product of the number of slave processes and the number of particles per slave results in the total number of particles accounted for in the simulation. Table 4 lists the details for simulations of experiment SP1 for a polymerization of 60 min with the number of particles and slaves as well as the time required for computing. The ensemble size varied from 16 000 to 512 000 particles with 16 or 64 slaves. The compute server used consists of a total of 16 hardware cores, which were used to full capacity exclusively for the simulations introduced here.

Fig. 10 demonstrates a linear increase in computing time with the number of particles. This finding reveals that the master-slave concept chosen is perfectly suited for parallelization of the simulation. The memory required for each particle in the kMC simulation increases with monomer conversion to around 125 kB, which depends on the particle size and the number of

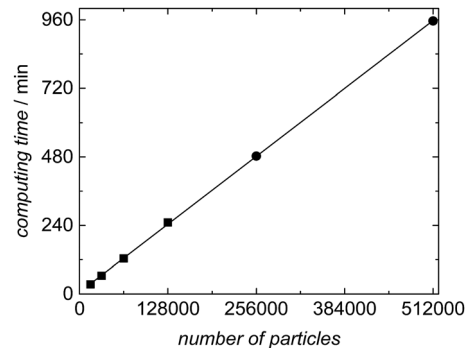


Fig. 10 Correlation between computing time and number of particles for the simulation of experiment SP1 with a reaction time of 60 min. Further details are contained in Table 4.

polymer chains inside the particle. Thus, the memory requirement of 8 GB for an ensemble size of 64 000 particles may be considered as moderate.

## Summary

The holistic modeling approach introduced for an *ab initio* kMC simulation of seeded emulsion polymerization enables to model a large ensemble of particles due to parallelization. The number of particles involved, and thus, the sample size can be selected freely depending on the requested result. Typically ensembles of 64 000 were used for modeling. Additionally, simulations were performed up to 512 000 particles.

The simulation was successfully applied to the seeded emulsion polymerization of styrene. A termination model was used, which allows for the calculation of an individual termination rate coefficient in each MC step for every macroradical in a particle. The termination model considers the individual chain-length dependence of each radical and accounts for the variation of the termination rate coefficient with the polymer content in the particle. Each particle is simulated as a nanoreactor of realistic size. Therefore, it is possible to apply current kinetic models for  $k_t$  derived for bulk polymerizations<sup>37,38</sup> to emulsion polymerizations. The simulation results were validated on the basis of experimental data. Very good agreement with respect to conversion vs. time data and molar mass distributions was observed using kinetic parameters published without any adjustments of these parameters. It is shown that the simulation is sensitive to particle size distribution and styrene concentration in the particles. This new kMC modeling approach allows for deep insight into the molar mass distribution in individual particles. The simulations allow to establish correlations between particle size, conversion and molar mass distribution. This information may be derived for individual particles or pre-defined subsets of particles. In future, the validated model will be used for more complex polymerization systems.

## Conflicts of interest

There are no conflicts of interest to declare.

Table 4 Computing time for the simulation of experiment SP1 with a reaction time of 60 min and the indicated number of particles in a master-slave simulation process with 16 or 64 parallel slave processes

Particles	Slaves	Particles per slave	Computing time, min
16 000	16	1000	34
32 000	16	2000	64
64 000	16	4000	124
128 000	16	8000	250
256 000	64	4000	483
512 000	64	8000	956



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