Value Simulation of the Interacting Pair Number for Solution of the Monodisperse Coagulation Equation

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Problem Statement and General Information

- Let us consider an initial value problem for the Smoluchowski equation:

$$\frac{\partial n_l(t)}{\partial t} = \frac{1}{2}\sum_{i+j=l} k_{ij} n_i(t)\, n_j(t) - \sum_{i \geqslant j} k_{il} n_i(t)\, n_l(t), \quad n_l(0) = n_l^{(0)}$$

$n_l(t)$ - average number of l-sized particles in the system at the time instant t;

$k(i,j)$ - coagulation coefficients.

Problem Statement and General Information

- **Integral equation** in transformed phase space

$Z = (X, \pi)$, $X = (N, l_1, \cdots, l_N)$ [2]

$$F(Z,t) = \int_0^t \int_{\mathbb{Z}} F(Z',t') K(Z',t' \rightarrow Z,t)\, \mathtt{d}Z'\, \mathtt{d}t' + F_0(Z)\delta(t)$$

where $dZ = dX\, d\mu_0(\pi)$

Problem Statement and General Information

- The kernel K of the latter integral equation has **multiplicative structure**

$$K(Z', t' \to Z, t) = k(t' \to t|X')\frac{a(\pi)}{A(X')}K_1(X' \to X|\pi)$$

where $k(t' \to t|X') = A(X')\exp\{-(t-t')A(X')\}$

- $K_1(X' \to X|\pi)$ defines transformation of the system after collision of the pair $\pi = (i,j)'$.

- Collision of the particles i and j results in their replacement by a particle of the size $l_i + l_j$, and the number of particles reduces by one.

$$N = N' - 1; X = (N, l_1, \cdots, l_N), \quad N \leqslant N_0, \quad l_i \in \overline{1, N_0}$$

Problem Statement and General Information

- We will estimate the **functionals** of the particle flux $\Phi(X,t)$:

$$J_H(t) = \int H(X)\Phi(X,t)dX = \int_0^t \int_Z \tilde{H}(X,t-t')F(Z,t')dZdt'$$

$$H(X) \in L_\infty, \quad \widetilde{H}(X,t) = H(X)\exp\{-tA(X)\}$$

Problem Statement and General Information

- Let us denote a **Markov chain** (Z_n, t_n) , $n \in 0, 1, \ldots \nu$ with normalized density of the initial state

$$P_0(Z, t) = P_0(Z)\delta(t)$$

and normalized transition density

$$P(Z', t' \to Z, t) = p(t' \to t|X')P_1(\pi|X')P_2(X' \to X|\pi)$$

- **Random weights** are defined by the formulas:

$$Q_0 = F_0(Z)/P_0(Z), \qquad Q_n = Q_{n-1}Q(Z_{n-1}, t_{n-1}; Z_n, t_n)$$

$$Q(Z_{n-1}, t_{n-1}; Z_n, t_n) = K(Z', t' \to Z, t)/P(Z', t' \to Z, t)$$

Problem Statement and General Information

- A **weight collision estimator** will be used to estimate the functionals:

$$\xi = \sum_{i=0}^{\nu} Q_n \tilde{H}(X_n, T - t_n) \quad \nu = \max\{n : t_n < T,\ n = 0, 1, \ldots, N_0 - 1\}$$

- Further we will estimate two functionals:

$J_H^{(1)}(T) \approx n_1(T)$ - monomer concentration in the system;

$J_H^{(12)}(T) = J_H^{(1)}(T) + J_H^{(2)}(T)$ - monomer and dimer concentration in the system at the time instant T.

Analytic Solution of the Test Problem with Linear Coefficients

- **Test problem** for Smoluchowski equation

$K_{ij} \equiv a + b(i+j)/2$ - coagulation coefficients

$n_l(t=0) = \delta_{l,1}, \quad l \geq 1$ - initial distribution

- For this problems parameters of simulation can be obtained analytically:

$$A(X) = \frac{(N-1)}{2}\left[a\frac{N}{N_0} + b\right]$$

$$a(\pi) \equiv a(N, l_i, l_j) = \frac{2a + b(l_i + l_j)}{2N_0}$$

Analytic Solution of the Test Problem with Linear Coefficients

- **Analytical solution** [6] for the problem considered:

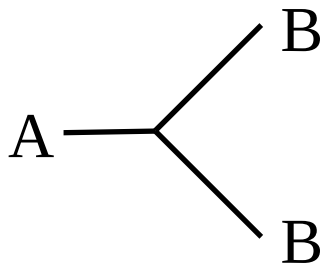
$$n_1(\mu(t)) = \mu \cdot \left(\frac{a\mu + b}{a + b}\right)^{1+b/a}$$ - monomer concentration;

$$n_2(\mu(t)) = \mu \cdot (1 - \mu) \cdot \left(\frac{a\mu + b}{a + b}\right)^{1+2b/a}$$ - dimer concentration;

$$\mu(t) = \frac{b}{(a + b)\exp\{bt/2\} - a}$$

Explanation of the Model $A \quad R \quad B_{f-1}$

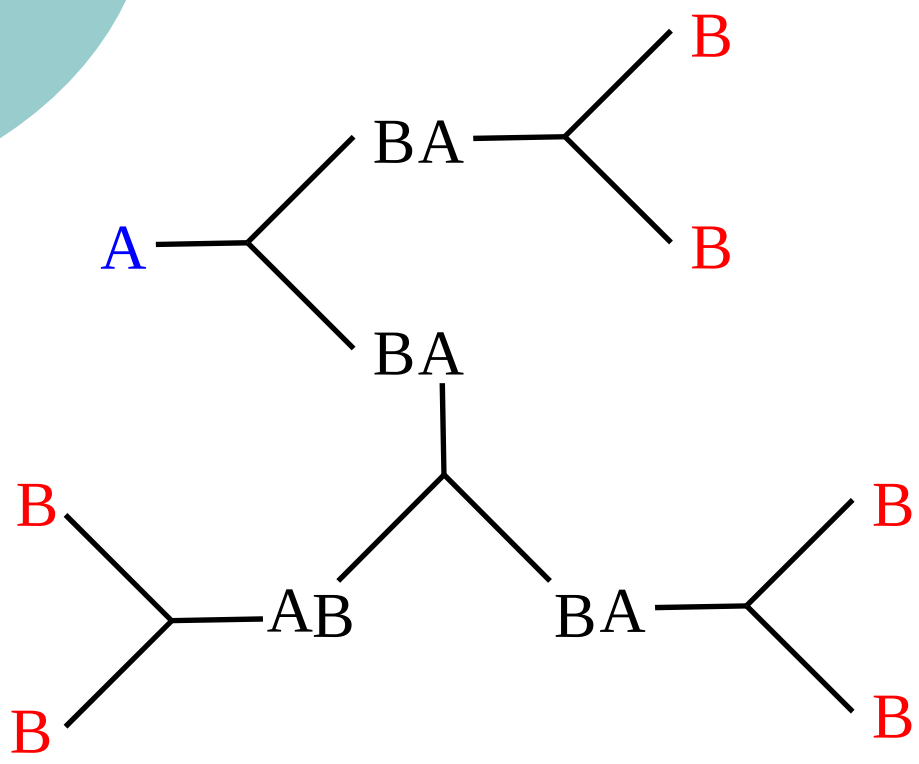
- The following type of molecules we consider as **monomers** *(in this figure is shown a model of monomer for f=3)*

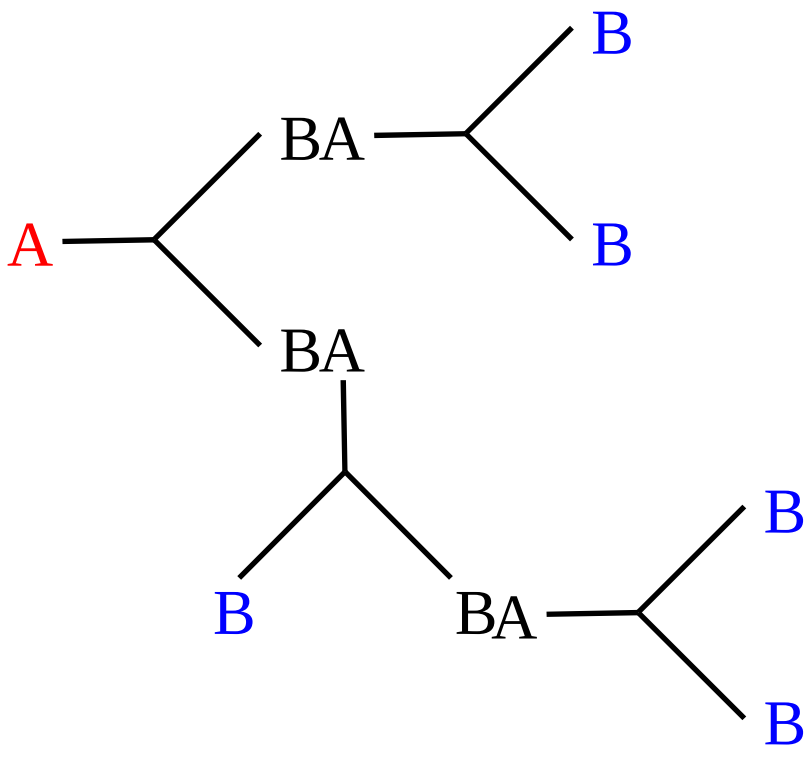


- Units of **A**-type condense with units of **B-**type, but reactions between the same units are forbidden.

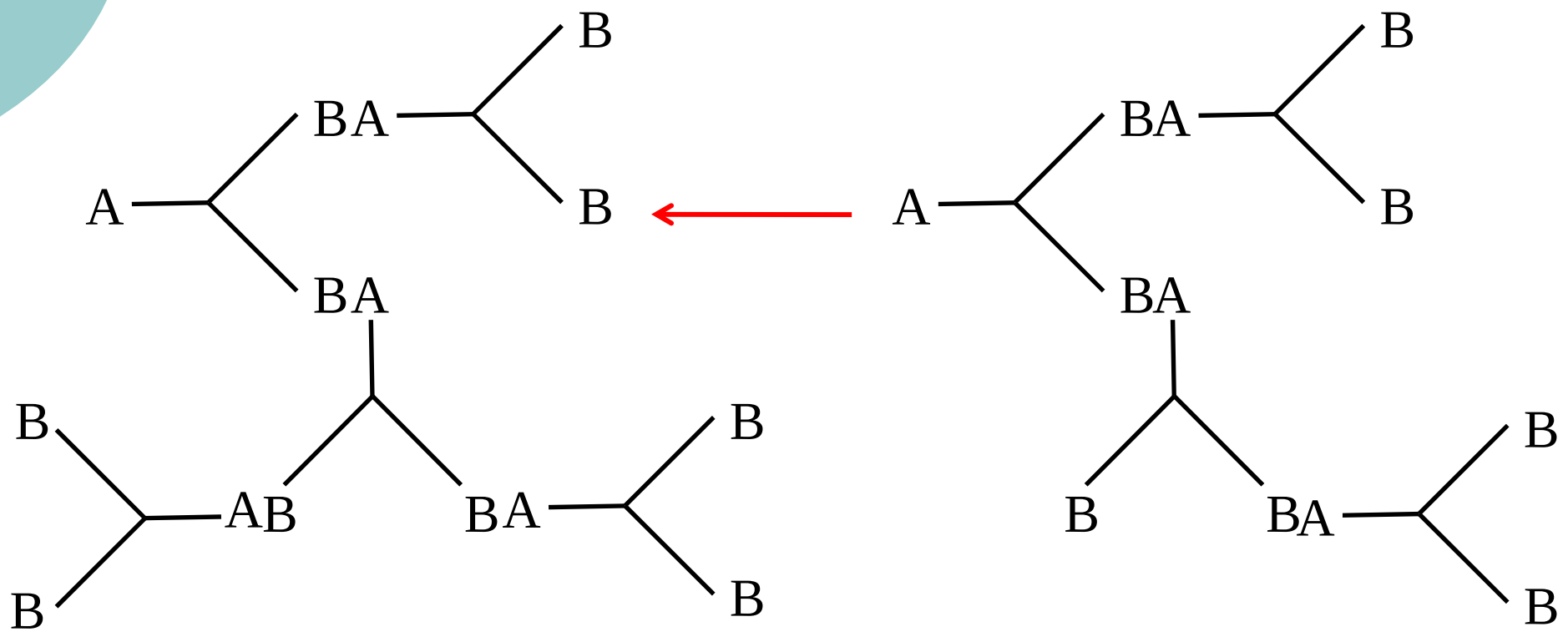
- We neglect reactions between units of **A**-type and **B**-type within a multimer (to avoid cyclization) and steric hindrance.

Explanation of the Model





Explanation of the Model



Explanation of the Model

- A multimer contains:
  - unreacted units of A-type – 1;
  - unreacted units of B-type for a *k-meric* particle – $(f-2)k+1$
- As a result, the probability for the particles *i* and *j* to interact is proportional to $(i+j)(f-2)+2$, and the **coagulation coefficient** has the following form:

$$K_{ij} = a + b(i+j)/2$$

Value Simulation of the Interacting Pair Number for Monomers

- The value function $\varphi^*(X,t)$ is defined as a value of functional J_H calculated on a source function $\delta(X'-X)\delta(t'-t)$

  which means that

$$\varphi^*(X,t) = \mathrm{E}\xi_{(X,t)}$$

  where

$$\xi_{(X,t)} = \tilde{H}(X, T-t) + \sum_{n=1}^{\nu} Q_n \tilde{H}(X_n, T-t_n)$$

Value Simulation of the Interacting Pair Number for Monomers

- Let us denote:

  N' – total number of particles in the ensemble;

  N'_1 – number of monomers in the ensemble.

- Each of all possible interacting pairs falls into one of the following non-overlapping subsets $\pi_1 \cup \pi_2 \cup \pi_0$:

π_1 – contains 'minus-1-pairs' of the form {*monomer, multimer*}

π_2 – contains 'minus-2-pairs' of the form {*monomer, monomer*}

π_0 – contains 'minus-0-pairs' of the form {*multimer, multimer*}

$$\mathcal{N}_1 = N'_1(N' - N'_1);\ \mathcal{N}_2 = \frac{N'_1(N'_1 - 1)}{2};\ \mathcal{N}_0 = \frac{(N' - N'_1)(N' - N'_1 - 1)}{2}.$$

Value Simulation of the Interacting Pair Number for Monomers

- Let us rewrite physical density distribution

$$\mathcal{P}_0(i,j) = \frac{2a + b(l_i + l_j)}{aN(N-1) + bN_0(N-1)}$$

of the interacting pair number in the following randomized form:

$$1 \equiv \sum_{\pi} \frac{2}{N'(N'-1)} = p_1 \sum_{\pi_1} f_1(i,j) + p_2 \sum_{\pi_2} f_2(i,j) + p_0 \sum_{\pi_0} f_0(i,j)$$

p_{m} – probability to choose the subset π_{m};

$f_{\mathrm{m}}(i,j)$ – probability to choose pair (i,j) from the subset π_{m}.

Value Simulation of the Interacting Pair Number for Monomers

- The probabilities to choose a certain subset have the following form:

$$p_2 = \frac{N_1'(N_1'-1)}{N'-1} \cdot \frac{a+b}{aN'+bN_0},$$

$$p_1 = \frac{N_1'}{N'-1} \cdot \frac{2a(N'-N_1') + b(N_0+N'-2N_1')}{aN'+bN_0}$$

$$p_0 = \frac{(N'-N_1'-1)}{N'-1} \cdot \frac{a(N'-N_1') + b(N_0-N_1')}{aN'+bN_0}$$

Value Simulation of the Interacting Pair Number for Monomers

- Simulation of particles within certain subsets:

- **monomers** are uniformly chosen within π_1 and π_2;

- **multimers** are chosen within π_1 and π_0 according to physical probabilities, which have the following form:

  - monomer-multimer:

$$\mathcal{P}_j = \frac{2a + b(1 + l_j)}{2a(N' - N_1') + b(N_0 + N' - 2N_1')}.$$

  - multimer-multimer:

$$\mathcal{P}_j = \frac{2a(N' - N_1' - 1) + b(N_0 - N_1') + bl_j(N' - N_1' - 2)}{2(N' - N_1' - 1)[a(N' - N_1') + b(N_0 - N_1')]}$$

Value Simulation of the Interacting Pair Number for Monomers

- In order to "preserve" the monomers in the system, we will simulate the interacting pair number using probabilities q_{m}, which are proportional to the number of monomers left in the system, instead of p_{m}:

$$q_1 = \frac{p_1(N_1' - 1)}{C}, \quad q_2 = \frac{p_2(N_1' - 2)}{C}, \quad q_3 = \frac{p_3 N_1'}{C}$$

$$C = \mathbf{E}(N_1) = N_1' \cdot \frac{N' - 2}{N' - 1}\left(1 - \frac{a + b}{aN' + bN_0}\right).$$

- This modification is taken into consideration when the random weight is calculated:

$$Q = Q' \frac{p_{\mathrm{m}}}{q_{\mathrm{m}}}$$

Value Simulation of the Interacting Pair Number for the Sum of Monomers and Dimers

- Denote also N_2' – number of dimers in the ensemble.

- Non-overlapping subsets splitting the set of all possible interacting pairs:

π_{11} – contains 'minus-1-pairs' of the form $\{monomer,\ monomer\}$

π_{1k} – contains 'minus-1-pairs' of the form $\{monomer,\ multimer\}$

π_{2k} – contains 'minus-1-pairs' of the form $\{dimer,\ multimer\}$

π_{22} – contains 'minus-2-pairs' of the form $\{dimer,\ dimer\}$

π_{12} – contains 'minus-2-pairs' of the form $\{monomer,\ dimer\}$

π_{kk} – contains 'minus-0-pairs' of the form $\{multimer,\ multimer\}$

Value Simulation of the Interacting Pair Number for the Sum of Monomers and Dimers

- Let us represent the “physical” distribution density of the interacting pair number in the form, similar to the case of monomers:

$$1 \equiv \sum_{\pi} \mathcal{P}_0(i,j) = p_{11} \sum_{\pi_{11}} f_{11}^{(i,j)} + p_{1k} \sum_{\pi_{1k}} f_{1k}^{(i,j)} + p_{2k} \sum_{\pi_{2k}} f_{2k}^{(i,j)} + \\ + p_{12} \sum_{\pi_{12}} f_{12}^{(i,j)} + p_{22} \sum_{\pi_{22}} f_{22}^{(i,j)} + p_{kk} \sum_{\pi_{kk}} f_{kk}^{(i,j)},$$

p_{mn} – probability to choose the subset π_{mn} ;

$f_{\mathrm{mn}}^{(i,j)}$ – probability to choose the pair (i,j) from the subset π_{mn} .

Value Simulation of the Interacting Pair Number for the Sum of Monomers and Dimers

- The probabilities to choose a certain subset have the following form :

$$p_{11} = \frac{N_1'(N_1'-1)}{N'-1} \cdot \frac{a+b}{aN'+bN_0},$$

$$p_{12} = \frac{N_1'N_2'}{N'-1} \cdot \frac{2a+3b}{aN'+bN_0},$$

$$p_{22} = \frac{N_2'(N_2'-1)}{N'-1} \cdot \frac{a+2b}{aN'+bN_0},$$

$$p_{1k} = \frac{N_1'}{N'-1} \cdot \frac{2a(N'-N_1'-N_2')+b(N_0+N'-2N_1'-3N_2')}{aN'+bN_0},$$

$$p_{2k} = \frac{N_2'}{N'-1} \cdot \frac{2a(N'-N_1'-N_2')+b(N_0+2N'-3N_1'-4N_2')}{aN'+bN_0},$$

$$p_{kk} = \frac{N'-N_1'-N_2'-1}{N'-1} \cdot \frac{a(N'-N_1'-N_2')+b(N_0-N_1'-2N_2')}{aN'+bN_0},$$

Value Simulation of the Interacting Pair Number for the Sum of Monomers and Dimers

- Simulation of particles within certain subsets:

- **monomers** are uniformly chosen within corresponding groups;
- **multimers** are chosen within π_{1k}, π_{2k} and π_{kk} according to physical probabilities $\mathcal{P}_j$, $j = N_1' + N_2' + 1, \ldots, N'$, which have the following form:
  - monomer-multimer:
$$\mathcal{P}_j = \frac{2a + b(1 + l_j)}{2a(N' - N_1' - N_2') + b(N_0 + N' - 2N_1' - 3N_2')}.$$
  - dimer-multimer:
$$\mathcal{P}_j = \frac{2a + b(2 + l_j)}{2a(N' - N_1' - N_2') + b(N_0 + 2N' - 3N_1' - 4N_2')}$$
  - multimer-multimer:
$$\mathcal{P}_j = \frac{2a(N' - N_1' - N_2' - 1) + b[(N_0 - N_1' - 2N_2') + l_j(N' - N_1' - N_2' - 2)]}{2(N' - N_1' - N_2' - 1)[a(N' - N_1' - N_2') + b(N_0 - N_1' - 2N_2')]}$$

Value Simulation of the Interacting Pair Number for the Sum of Monomers and Dimers

- In order to "preserve" the monomers and dimers in the system, we will simulate the interacting pair number using probabilities q_{mn}, which are proportional to the sum of monomers and dimers left in the system, instead of p_{mn} :

$$q_{11} = (N_1' + N_2' - 1)\frac{p_{11}}{C}; \quad q_{1k} = (N_1' + N_2' - 1)\frac{p_{1k}}{C}; \quad q_{2k} = (N_1' + N_2' - 1)\frac{p_{2k}}{C};$$

$$q_{12} = (N_1' + N_2' - 2)\frac{p_{12}}{C}; \quad q_{22} = (N_1' + N_2' - 2)\frac{p_{22}}{C}; \quad q_{kk} = (N_1' + N_2' - 0)\frac{p_{kk}}{C};$$

$$C = (N_1' + N_2') \cdot \frac{N' - 2}{N' - 1}\left(1 - \frac{a + 2b}{aN' + bN_0}\right) + N_1'\frac{a(N_1' - 1) + b(N' + N_1' - 3)}{(N' - 1)(aN' + bN_0)}$$

- This modification is taken into consideration when the random weight is calculated: $Q = Q'\frac{p_{mn}}{q_{mn}}$

Results of Numerical Experiments

Table 1. Estimation of $J_{H_1}(T)$ for $\mathbf{a} = 1$, $\mathbf{b} = 2$ $(T = 0.1; 1; 4; 10)$.

Simulation	$\tilde{J}_{H_1}(T)$	$\bar{\sigma}$	RE (%)	t_c	S_d/S_v
$n_1(0.1) = 7.5131 \cdot 10^{-1}$ $(T = 0.1;\ M = 10^4;\ N_0 = 10^3)$					
direct	$7.5053 \cdot 10^{-1}$	$2.9 \cdot 10^{-4}$	0.10	4.8	$--$
value	$7.5155 \cdot 10^{-1}$	$2.0 \cdot 10^{-4}$	0.03	5.5	**1.79**
$n_1(1) = 1.2263 \cdot 10^{-1}$ $(T = 1;\ M = 10^4;\ N_0 = 10^3)$					
direct	$1.2266 \cdot 10^{-1}$	$1.1 \cdot 10^{-4}$	0.02	37.7	$--$
value	$1.2271 \cdot 10^{-1}$	$4.7 \cdot 10^{-5}$	0.07	34.9	**6.09**
$n_1(4) = 3.7076 \cdot 10^{-3}$ $(T = 4;\ M = 10^4;\ N_0 = 10^2)$					
direct	$3.6648 \cdot 10^{-3}$	$3.0 \cdot 10^{-5}$	1.16	15.2	$--$
value	$3.6925 \cdot 10^{-3}$	$1.2 \cdot 10^{-5}$	0.41	15.9	**6.27**
$n_1(10) = 8.9684 \cdot 10^{-6}$ $(T = 10;\ M = 10^5;\ N_0 = 2 \cdot 10^2)$					
direct	$9.4500 \cdot 10^{-6}$	$6.9 \cdot 10^{-7}$	5.37	68.9	$--$
value	$8.6176 \cdot 10^{-6}$	$5.4 \cdot 10^{-8}$	3.91	74.9	**152**

Results of Numerical Experiments

Table 2. Estimation of $J_{H_{12}}(T)$ for $\mathbf{a} = 1$, $\mathbf{b} = 2$ $(T = 0.1; 1; 4; 10)$.

Simulation	$\tilde{J}_{H_{12}}(T)$	$\bar{\sigma}$	RE (%)	t_c	S_d/S_v
$n_1(0.1) + n_2(0.1) = 8.4460 \cdot 10^{-1}$ $(T = 0.1;\ M = 10^4;\ N_0 = 10^3)$					
direct	$8.4363 \cdot 10^{-1}$	$3.4 \cdot 10^{-4}$	0.12	4.6	—
value	$8.4516 \cdot 10^{-1}$	$1.6 \cdot 10^{-4}$	0.07	5.3	**3.85**
$n_1(1) + n_2(1) = 1.7364 \cdot 10^{-1}$ $(T = 1;\ M = 10^4;\ N_0 = 10^3)$					
direct	$1.7379 \cdot 10^{-1}$	$1.4 \cdot 10^{-4}$	0.08	25.9	—
value	$1.7388 \cdot 10^{-1}$	$6.8 \cdot 10^{-5}$	0.13	28.9	**3.58**
$n_1(4) + n_2(4) = 5.3553 \cdot 10^{-3}$ $(T = 4;\ M = 10^4;\ N_0 = 10^2)$					
direct	$5.3443 \cdot 10^{-3}$	$3.6 \cdot 10^{-5}$	0.21	13.5	—
value	$5.3564 \cdot 10^{-3}$	$1.5 \cdot 10^{-5}$	0.02	15.1	**5.37**
$n_1(10) + n_2(10) = 1.2954 \cdot 10^{-5}$ $(T = 10;\ M = 10^5;\ N_0 = 2 \cdot 10^2)$					
direct	$1.3600 \cdot 10^{-5}$	$8.3 \cdot 10^{-7}$	5.37	64.1	—
value	$1.2594 \cdot 10^{-5}$	$7.2 \cdot 10^{-8}$	2.78	72.5	**117**

Results of Numerical Experiments

Table 3. Estimation of $J_{H_1}(T)$ and $J_{H_{12}}(T)$ for $\mathbf{a} = 2$, $\mathbf{b} = 10$.

Simulation	$\tilde{J}_H(T)$	$\bar{\sigma}$	RE (%)
$n_1(10) = 5.3828 \cdot 10^{-23}$ $(T = 10;\ M = 10^6;\ N_0 = 10^3)$			
value	$5.3047 \cdot 10^{-23}$	$1.9 \cdot 10^{-25}$	1.45
direct	**0.0**	$--$	**100**
$n_1(10) + n_2(10) = 7.5460 \cdot 10^{-23}$ $(T = 10;\ M = 10^6;\ N_0 = 10^3)$			
value	$7.4278 \cdot 10^{-23}$	$2.1 \cdot 10^{-25}$	1.57
direct	**0.0**	$--$	**100**

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THANK YOU!