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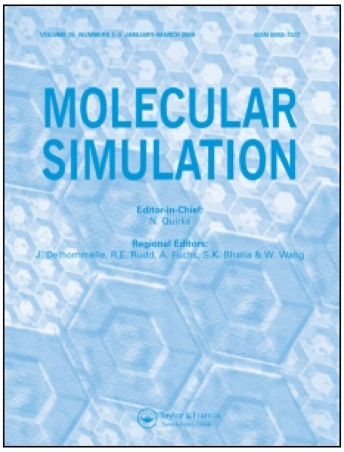

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New version of Monte Carlo expanded ensemble method for precise calculations of free energy difference

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A new version of Monte Carlo (MC) expanded ensemble (EE) method is proposed for the calculations of free energy difference (FED) between two different systems with close values of the free energy. In order to check the method the FED between simple model systems (fluid of hard spheres and freely jointed polymer chain of hard spheres) was calculated. The free energy of the mentioned above systems was also calculated by a standard MC EE method in order to compare the results of two simulations. It was shown that the accuracy of a new algorithm is the same as of a standard one. At the same time new version of EE allows us to obtain FED between two systems having quite different structures, but similar free energies, during one simulation run.

Keywords: Monte Carlo; Free energy calculation; Expanded ensemble; Helmholz FED

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1. Introduction

Calculations of such thermodynamic functions as free energy, chemical potential, entropy are very important for the physical chemistry of solutions. These properties are of special interest for the understanding of many molecular phenomena (e.g. chemical equilibrium, solvation, phase transitions, etc.) and in many cases Monte Carlo (MC) method offers the only convenient way to calculate them. However, in the standard MC scheme the calculations of entropy-depending properties is impossible due to the absence of the appropriate function of the given microstate (the estimator) to be averaged. It is well-known that Helmholtz free energy F is directly related to the canonical partition function Z, but the precise estimation of the latter is impossible within the standard MC procedure. There exist a number of different methods (particle insertion [1], multistage sampling [2], acceptance ratio [3], umbrella sampling [4], perturbation theory [5], thermodydamic integration [6], expanded ensemble [7]) to calculate Helmholz free energy, entropy of the system, chemical potentials of the components, etc. (see also reviews [8–10]). Each of these methods has its advantages and disadvantages, but they all have a common feature: results with high accuracy require long simulation runs. This problem can be especially severe for calculations of small differences in free energy between two systems. This is often the case for the objects of soft matter science, which has been developing rapidly during the last decade. For such systems as block-copolymer gels, micellar solutions, etc. small changes of external conditions (and thus, in the free energy) can lead to considerable changes in the mesostructure, and it results in drastic changes of the system properties. In this paper we propose a new version of expanded ensemble (EE) MC method, which would hopefully allow us to decrease the error in the estimation of free energy difference (FED) for two complex systems with values of the free energy close to each other.

Originally our aim was to determine the relative stability of the micelles of two forms (spherical and cylindrical ones) at different condition using MC method. It is well known that it is necessary to compare the free energies of two systems in order to estimate their relative stability, so the goal of the work was to calculate FED of these forms of micelles. The micelles are rather large molecular aggregates and their free energy in absolute value is very high. At the same time the specific free

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energies of spherical and cylindrical micelles in the range of the second critical micellization concentration (CMC2, when spherical micelles change to cylindrical ones) are very close to each other, so that the form of the micelle can easily change. It means that around CMC2 the value of FED between the micelles of two forms is rather small in comparison to the value of the free energy of a micelle itself that can cause substantial errors in calculations. Among known methods of calculation of the free energy we have chosen MC EE method as a very powerful and flexible one. The version of this method elaborated in this paper is tested for rather simple and thoroughly studied systems, the results of the calculations for micellar solutions will be presented later.

2. Calculation methods

MC EE method [7] is based on the introduction of the new ("expanded") partition function:

$$Z = \sum_{m=1}^{M} Z_m(\gamma_m;\ldots)\exp(\psi_m) \tag{1}$$

where $Z_m(\gamma_m;\ldots)$ is the configuration integral of the m-th subensemble, ψ_m is the preweighting factor, γ_m is the extension parameter of the ensemble. It can either coincide with some thermodynamic parameter (temperature, pressure, number of particles, etc.) or can be any other characteristic of the system (intermolecular potential well depth, etc.). The system being considered is simulated in the new ensemble extended by the parameter γ_m. Two types of steps usually exist in the corresponding MC procedure: the change of the positions of the particles inside the chosen subensemble at a given value of γ_m, and the transition of the system into the neighboring subensemble at fixed positions of the particles. The probability to accept a step $(i \to j)$ is $p_{i\to j} = \min\{1, \exp(\beta H_i - \beta H_j - \psi_i + \psi_j)\}$, where β is the reciprocal temperature, H_k is the Hamiltonian of the k-th subensemble. The probability p_i for the system to stay in the i-th subensemble is calculated in the simulations. On the other hand, it is evident that $p_i = Z_i \exp(\psi_i)/Z$. So, as long as $\beta_i F_i = -\ln Z_i$ for the i-th subensemble, one can get the relation:

$$\frac{p_i}{p_j} = \frac{Z_i}{Z_j}\exp(\psi_i - \psi_j) = \exp(-\beta_i F_i + \beta_j F_j + \psi_i - \psi_j). \tag{2}$$

The latter is used for the calculations of the Helmholz FED between any pair of subensembles in the system.

Let us consider two systems: A and B. For each of them we shall take into account two states: the one under investigation (1), and the other with the known free energy (0) (reference system). The configurational Hamiltonian depending on the parameter $\gamma_m (1 \le m \le M)$ is introduced: $H_A(q_A, \gamma_m)$ and $H_B(q_B, \gamma_m)$, so that for each system $H(q, \gamma_1) = H^{(0)}$ and $H(q, \gamma_M) = H^{(1)}$. If we are interested in FED for two systems each of them being in the state (1) then the standard way to carry out two separate EE calculations is:

$$Z_A = \sum_{m=1}^{M} Z_{A,m} e^{\psi_{A,m}}, \quad Z_B = \sum_{m=1}^{M} Z_{B,m} e^{\psi_{B,m}} \tag{3}$$

$$\begin{aligned} \frac{Z_{A,M}}{Z_{A,1}}\frac{e^{\psi_{A,M}}}{e^{\psi_{A,1}}} &= \frac{p_{A,M}}{p_{A,1}} = e^{\beta F_{A,1} - \beta F_{A,M} + \psi_{A,M} - \psi_{A,1}}, \\ \frac{Z_{B,M}}{Z_{B,1}}\frac{e^{\psi_{B,M}}}{e^{\psi_{B,1}}} &= \frac{p_{B,M}}{p_{B,1}} = e^{\beta F_{B,1} - \beta F_{B,M} + \psi_{B,M} - \psi_{B,1}} \end{aligned} \tag{4}$$

$$\begin{aligned} \beta F_{A,M} &= \beta F_{A,1} + \psi_{A,M} - \psi_{A,1} - \ln\frac{p_{A,M}}{p_{A,1}}, \\ \beta F_{B,M} &= \beta F_{B,1} + \psi_{B,M} - \psi_{B,1} - \ln\frac{p_{B,M}}{p_{B,1}} \end{aligned} \tag{5}$$

$$\begin{aligned} \beta F_A^{(1)} - \beta F_B^{(1)} = \beta F_{A,M} - \beta F_{B,M} = \beta F_A^{(0)} - \beta F_B^{(0)} + \psi_{A,M} \\ - \psi_{A,1} - \psi_{B,M} + \psi_{B,1} - \ln\frac{p_{A,M}}{p_{A,1}} + \ln\frac{p_{B,M}}{p_{B,1}}. \end{aligned} \tag{6}$$

Now let us introduce a new version of the EE method. Let $H_{A,m} = (1 - \gamma_{A,m})H_A^{(0)} + \gamma_{A,m}H_A^{(1)}$ and $H_{B,m} = \gamma_{B,m}H_B^{(0)} + (1 - \gamma_{B,m})H_B^{(1)}$; $0 \le \gamma_{A,m} \le 1$, $0 \le \gamma_{B,m} \le 1$, $1 \le m \le M$. The expanded partition function for the combined system can be introduced as follows:

$$Z = \sum_{m=1}^{M} Z_{A,m} Z_{B,m} e^{\psi_m} \tag{7}$$

where $Z_{A,m} = \int e^{-\beta H_{A,m}} \mathrm{d}q_A$, and $Z_{B,m} = \int e^{-\beta H_{B,m}} \mathrm{d}q_B$ are the canonical partition functions of the systems A and B, correspondingly. The probability for the system to be found in the state (q_A, q_B) (the probability of a microstate of the combined system) in the subensemble m can be obtained from the relation: $p_m(q_A, q_B) = \exp(-\beta(H_{A,m}(q_A) + H_{B,m}(q_B) + \psi_m))/Z$. The averaged probability (over the configurational space) to find the system in the m-th subensemble is as follows $p_m = \int p_m(q_A, q_B)\mathrm{d}q_A \mathrm{d}q_B / Z = Z_{A,m}Z_{B,m}e^{\psi_m}/Z$. Then $\beta F_M - \beta F_1 = \psi_M - \psi_1 - \ln p_M/p_1$. But as long as $\beta F_1 = \beta F_A^{(0)} + \beta F_B^{(1)}$ and $\beta F_M = \beta F_A^{(1)} + \beta F_B^{(0)}$, it is clear that:

$$\beta F_A^{(1)} - \beta F_B^{(1)} = \beta F_A^{(0)} - \beta F_B^{(0)} + \psi_M - \psi_1 - \ln\frac{p_M}{p_1}. \tag{8}$$

This way the calculation of FED can be carried out in a single MC run, which is one of the main advantages of the suggested method, yielding the decrease of the errors.

As it was stated above, the proposed method is elaborated specially for complicated systems, but it was necessary to test it for the simple and well studied cases. For this purpose we calculate separately the free energies for the fluid of hard spheres (HS) and for a freely jointed polymer chain of hard spheres (FJC) using the standard EE

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method (3)–(5) and their difference according to equation (6). Then the same FED values were calculated by the new version of the method (7)–(8). The obtained results were compared with each other and with the data from literature.

3. Models

3.1 Intermolecular potential

The interaction potential in both systems was chosen as follows:

$$E(r) = \begin{cases} 0, & \text{if} \quad r \geq 1 \\ E_{\max}(1 - r^2), & \text{if} \quad r < 1 \end{cases} \tag{9}$$

Simulations were carried out in the temperature expanded canonical ensemble [6], so we assume that $Z_m = \int \exp(-\beta_m H(q))\mathrm{d}q$ in equation (1). The value of the reciprocal reduced (RR) temperature changes slowly from one subensemble to the other in the range $0 \leq \beta_m \leq 1$. The value of $E_{\max}(E_{\max} = 10{,}000)$ was chosen high so that at $\beta = 1$ the particles behave as HS since they practically do not penetrate into each other due to the sharp growth of the potential (9) at $r < 1$. At $\beta = 0$ the interactions between the particles disappear, and the system becomes an ideal gas. The same approach was used in the simulations of FJC. The only difference for FJC is the existence of rigid bonds between the neighboring monomer particles. Thus, in the first case the result of the calculations is FED between the HS fluid and the ideal gas, while in the second—it is FED between a FJC and a phantom chain (freely jointed chain of points).

3.2 Reference systems

A number of equations of state exist for HS. We have chosen two of them: that of Percus-Yevick (10) [11] and Carnahan-Starling (11) [12], which are known to be very accurate, especially at low densities.

$$\frac{pV}{NkT} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \tag{10}$$

$$\frac{pV}{NkT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \tag{11}$$

Here p is the pressure, V is the volume, N is the number of particles, $\eta = (\pi/6)(N/V)\sigma^3$ is the packing factor, σ is the diameter of a hard sphere. Each equation was integrated in order to obtain the dependence of the free energy on density:

$$\Delta F = -\int_V^{\infty} \left(p - \frac{NkT}{V}\right)\mathrm{d}V \tag{12}$$

where $\Delta F = F_{\mathrm{hs}} - F_{\mathrm{ig}}$ is Helmholz FED between the fluid of HS F_{hs} and the ideal gas F_{ig}. It is known that the compressibility factor for the HS according to equation (10) is higher, and according to equation (11) is lower in comparison to the results of MD simulations [13]. It means that the exact value of the free energy is to be found between the values obtained from equations (10) and (11).

There exist no analytical equations for the estimation of the free energies for polymer chains, but the numerical data can be found in the paper [14], devoted to the calculations of entropy of different polymer chains by entropic sampling method [15,16]. It is easy to obtain FED from these data: $\beta\Delta F = -\Delta S$.

4. Details of the simulation procedure

4.1 Wang-Landau algorithm for the self-adjustment of preweighting factors

The choice of preweighting factors ψ_m in equation (1) significantly influence the efficiency of simulations in EE defining the probabilities of visits of different subensembles p_m. Values of ψ_m were adjusted using the Wang-Landau (WL) algorithm [16], which was originally elaborated for the precise calculations of the density of states of a system in entropic sampling MC method. The main idea of this method can be used in quite different areas of computational science.

Let us consider in detail WL algorithm for the choice of preweighting factors in our case. Some arbitrary values of ψ_m are taken as the initial ones and the simulations in the EE are carried out. At each step during the change of the subensemble a small positive value $\Delta\psi$ is subtracted from the value ψ_m, corresponding to the accepted subensemble (new or old). Then according to the condition $p_{i\to j} = \min\{1, \exp(\Delta_{ij}(\psi - \beta H))\}$ the probability of transition into this subensemble is decreased, which means that the probability to visit this subensemble also decreases. In this case the relative probability of visiting other subensembles increases. In other words the adjustment of the preweighting factors results in obtaining the similar rates of visits for all the subensembles. When the difference in p_m does not exceed 10%, the value of $\Delta\psi$ is being decreased, $\Delta\psi \to \Delta\psi{\cdot}a$, where $a < 1$ (we take $a = 0.5$ as in the original work [16]). After that a new series (a sweep) of calculation is carried out for further fine tuning of ψ_m. The whole procedure is repeated until the value of $\Delta\psi$ becomes negligibly small in comparison to ψ_m (10–15 orders smaller).

As long as only the differences between ψ_m are important it is possible to choose any value of ψ_0, e.g. it can be taken equal to zero. That is why in order to avoid the errors connected with the limited accuracy of the computer it is necessary to subtract the value of ψ_0 from each ψ_m at the end of each sweep.

4.2 Choice of the subensembles

The number of subensembles and the choice of RR temperatures (the dependence of β_m on m) are very

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important for simulations. It is evident that the more subensembles we use the more computer time we need to obtain the desired accuracy of calculations. On the other hand, too small number of subensembles could cause very low probability of transition to the neighboring subensembles that could also negatively affect the accuracy of the results. So, the choice of the optimum number of subensembles is extremely important. The choice of the RR temperatures of subensembles in each case has been done in accordance with the probability of the system to move from the given subensemble to the neighboring ones: in each case this value was chosen so as to provide transition probability between 10 and 40% (mainly 20–30%). When the RR temperatures were chosen, the tuning of the preweighting factors was carried out according to WL algorithm. After that the calculations of the free energy were performed with the obtained values of ψ_m.

5. Results and discussion

5.1 *Details of the free energy calculations*

In order to avoid errors in calculations of the free energy caused by the finite sampling the dependence of the free energy on the number of MC steps during the simulations has been plotted for all systems being studied. The example of such dependence is given in figure 1 for HS at the density $\rho = 0.6\ \sigma^{-3}$ with $N = 63$ in the periodic box. Substantial changes of the free energy, much larger than fluctuations, occur in the initial stage of the simulations. Later, after 30 million steps, it oscillates around the value of 127.78 kT.

In order to estimate the influence of the size of the basic cell on the obtained results the dependence of the specific free energy on the number of particles in the basic cell at a given value of density was presented in N^{-1} scale with further extrapolation to infinite $N(N^{-1} \rightarrow 0)$. Such calculations have been done for all densities of HS. The example of this analysis is given in figure 2 for the density $\rho = 0.4\ \sigma^{-3}$. The number of particles in the basic cell varied from 10 to 240.

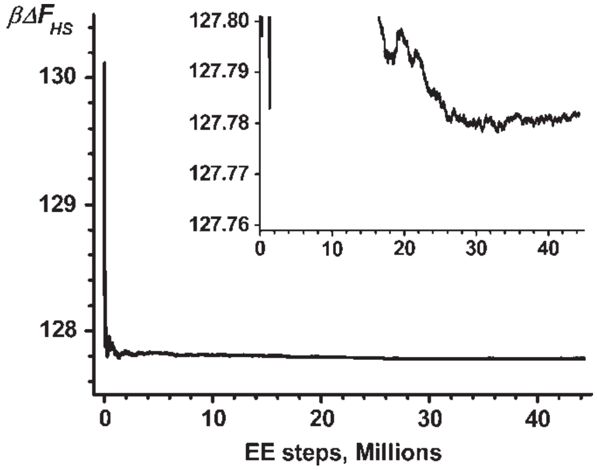

Figure 1. Dependence of FED on the number of MC simulation steps. Results shown are for HS, density $\rho = 0.6\ \sigma^{-3}$, $N = 63$.

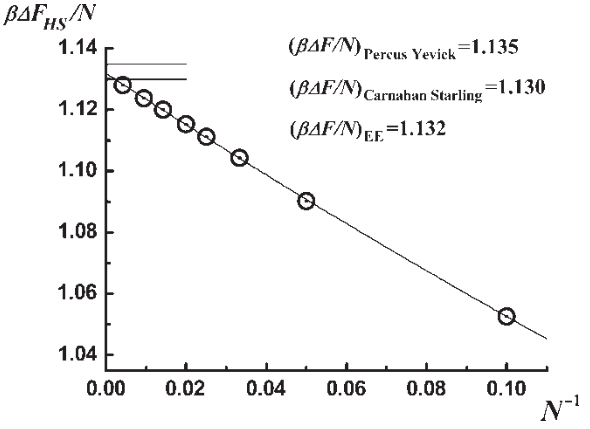

Figure 2. Dependence of FED for HS on the number of particles N in the simulation cell (circles). Density $\rho = 0.4\ \sigma^{-3}$.

As it is seen from figure 2 the value of FED for the infinite N ($N^{-1} \rightarrow 0$) is between the data determined from analytical approximations (10) and (11).

5.2 *Result for hard spheres fluid*

Free energies of the fluid of HS have been calculated in a wide range of densities, from 0.01 up to 0.8 σ^{-3} (figure 3, table 1). In all cases the values of FED calculated by EE MC method according to equations (3)–(5) are always between the values of theoretical approximations (10) and (11) (if there is any difference between them). It confirms the accuracy of our method. The simulations were repeated several times, and all the results given in the tables were reproduced with the same accuracy.

5.3 *Results for the polymer chain*

The dependence of specific free energy on the inverse number of monomers of the chain N(N varied from 5 to 150) is plotted in figure 4. The data of [14] are presented in the same figure for comparison. As it is seen the data

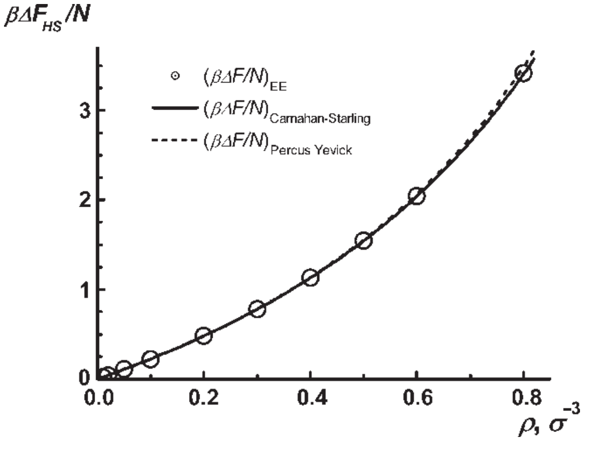

Figure 3. Dependence of FED for HS on the density. Circles—EE calculations. Lines—analytical approximations (10) and (11).

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Table 1. Comparison of EE results obtained in present work for HS fluid with the analytical approximations (equations (10) and (11)).

ρ, σ^{-3}	$\beta\Delta F_{HS}/N$ *Percus-Yevick*	$\beta\Delta F_{HS}/N$ *EE method*	$\beta\Delta F_{HS}/N$ *Carnahan-Straling*
0.01	0.0211	0.0211	0.0211
0.02	0.0424	0.0424	0.0424
0.05	0.1083	0.1083	0.1083
0.10	0.2241	0.2241	0.2241
0.20	0.4820	0.4818	0.4816
0.30	0.7820	0.7810	0.7801
0.40	1.135	1.132	1.130
0.50	1.556	1.546	1.544
0.60	2.066	2.046	2.042
0.80	3.485	3.419	3.403

correlate well. A slightly larger dispersion of points from [14] is most probably caused by poorer statistics in [14] for greater *N* compared to that of the present work.

5.4 Use of the new method in the EE calculations of FED

The calculations of FED between the HS fluid and the polymer chain ($\Delta F = \Delta F_{\mathrm{HS}} - \Delta F_{\mathrm{FJC}}$) have been carried out according to the scheme (7)–(8) in order to check the accuracy and efficiency of the new version of EE proposed in this work. The number of monomers in the chain and the number of particles of the HS fluid in the basic cell are taken equal. The EE has been constructed according to the following scheme. The first subensemble contained the fluid at $\beta = 1$ (i.e. HS fluid) and the polymer at $\beta = 0$ (i.e. a phantom chain). The last subensemble contained the fluid at $\beta = 0$ (i.e. ideal gas) and the polymer at $\beta = 1$ (i.e. a chain with hard core potential). So, $\Delta F = \Delta F_{\mathrm{HS}} - \Delta F_{\mathrm{chain}} = \psi_{\mathrm{first}} - \psi_{\mathrm{last}} + \ln(p_{\mathrm{last}}/p_{\mathrm{first}})$. The calculations of FED have been carried out for three different values of density: 0.1 0.2 0.4 particles/σ^3. The dependence of the specific free energy on the number of particles in the basic cell has been studied at each density (table 2). As it is seen from the table the results of two versions of EEs (new version proposed at the present work and the standard one [7]) almost coincide. The maximum difference between the data obtained according to these two versions did not exceed 0.5%.

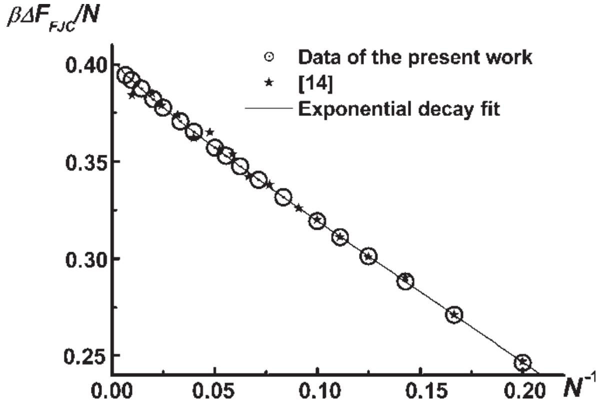

Figure 4. Comparison of the calculated FED of FJC obtained in the presented work (circles) with data from [14] (stars). Line—exponential decay fit.

Table 2. Comparison of the results ($\beta(\Delta F_{\mathrm{HS}} - \Delta F_{\mathrm{chain}})/N$) obtained by two versions of EE.

N	$\rho = 0.1$ *New*	$\rho = 0.1$ *[7]*	$\rho = 0.2$ *New*	$\rho = 0.2$ *[7]*	$\rho = 0.4$ *New*	$\rho = 0.4$ *[7]*
10	− 0.0842	− 0.0843	0.1530	0.1528	0.7655	0.7652
20	− 0.1256	− 0.1258	0.1215	0.1216	0.7505	0.7510
30	− 0.1412	− 0.1412	0.1093	0.1098	0.7455	0.7460
40	− 0.1495	− 0.1494	0.1032	0.1032	0.7423	0.7430
50	− 0.1546	− 0.1545	0.0990	0.0990	0.7400	0.7410
70	− 0.1608	− 0.1607	0.0936	0.0940	0.7373	0.7381
105	− 0.1657	− 0.1663	0.0895	0.0895	0.7352	0.7355

Thus, the new version of the method gives good results. From the analysis of the results it is difficult to say which of two methods is more accurate. It is connected with rather low values of FED for the polymer chain. We believe that the new version of the EE method could be very useful for the systems with quite close values of free energies. Another advantage of the new method is the possibility to perform one simulation run instead of two, which is more convenient and allows one to save computer time.

6. Conclusions

The new version of MC EE is proposed in this work. It allows us to decrease the error in the calculations of FED between two systems with close values of the free energy. The calculations of FED between the HS fluid and the freely joint polymer chain of HS has been carried out using this method. Explicit calculations for the same systems have been also performed according to the standard EE method. It was shown that the new version gives at least the same accuracy for the calculated FED in comparison to the original method, but it allows us to obtain the result during a single simulation run, thus saving computer time. For the first time WL algorithm was implemented for estimation of preweighting factors in EE method. The described method can be applied to complicated systems. At present the calculation of FED are being performed for the micelles of different form at various conditions to estimate their relative stability.

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