

# New approach to Monte Carlo calculation of the free energy: Method of expanded ensembles

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We propose a new effective Monte Carlo (MC) procedure for direct calculation of the free energy in a single MC run. The partition function of the expanded ensemble is introduced including a sum of canonical partition functions with a set of temperatures and additive factors (modification). Random walk in the space of both particle coordinates and temperatures provides calculation of free energy in a wide range of  $T$ . The method was applied to a primitive model of electrolyte including the region of low temperatures. In similar way other variants of expanded ensembles are constructed (e.g., over the number of particles  $N$  or volume  $V$ ). Its facilities in quantum statistics (path integral Monte Carlo) and some other applications are also discussed.

## I. INTRODUCTION

The principal difficulty in the Monte Carlo (MC) calculation of the free energy is the absence of corresponding microscopic analogue (estimator), i.e., a function of phase (or configuration) space variables to be averaged to obtain the required result. In further discussion (excluding Sec. V) "free energy" will mean its canonical configurational part, i.e.,

$$F = -kT \ln Z,$$

$$Z = (1/N!) \int_V dq \exp(-\beta H(q)) -$$

configurational integral,  $\beta = 1/kT$ ,  $H(q)$ —potential part of Hamiltonian,  $q$ —configuration variables. Formally one can write<sup>1</sup>

$$F = kT \ln[\langle \exp(\beta H) \rangle N! / V^N], \quad (1)$$

however, it is practically impossible to calculate the average of strongly varying quantity  $\exp(\beta H)$  in a finite MC run.<sup>1,2</sup>

Existing approaches deal with the calculation of the free energy difference (FED) or, equivalently, the ratio of partition functions  $Z_0/Z_1$ . A number of methods has been developed for the calculation of FED: particle insertion,<sup>3</sup> multi-stage sampling,<sup>4</sup> acceptance ratio method,<sup>5</sup> umbrella sampling,<sup>6</sup> perturbation theory,<sup>2</sup> and some others (e.g., see review in Ref. 7). The common point of these approaches is that systems "0" and "1" should not be too distantly separated in the configuration space. Thus for a system strongly differing from the reference system one should construct a chain of intermediate states and carry out separate MC simulations for each of them. The situation becomes worse for lower temperatures, higher density or greater number of particles in the MC cell.

We suggest here a new method for free energy calculation which can be carried out in a single MC run. In Sec. II we introduce a notion of the expanded (with the respect to temperature) canonical ensemble and describe the algorithm for computation of the free energy. Application of this method to restricted primitive model (RPM) of electrolyte and comparison of our results with those obtained in earlier

papers is presented in Sec. III. Section IV gives generalization of the present approach to other ensembles and shows the advantages of the suggested method. In Sec. V we discuss facilities of our approach in quantum statistics (path integral MC). Finally (Sec. VI) some other possible applications are discussed.

## II. TEMPERATURE EXPANDED CANONICAL ENSEMBLE

### A. General formulation

Consider an  $NVT$  ensemble with the Hamiltonian  $H(\{q_i\})$  and the reciprocal temperature  $\beta$ . Now introduce a set of  $\beta_m$ :

$$0 = \beta_0 > \beta_1 > \beta_2 > \dots > \beta_M = \beta. \quad (2)$$

For each  $\beta_m$  we have a canonical ensemble with the same Hamiltonian, fixed  $N$  and  $V$  and the partition function,

$$Z_m = \frac{1}{N!} \int \prod dq_i \exp(-\beta_m H\{q_i\}). \quad (3)$$

Next we create an expanded and modified ensemble with the partition function,

$$Z = \sum_{m=0}^M Z_m \exp(\eta_m), \quad (4)$$

where  $\eta_m$  are some constants to be discussed and chosen later. The expansion of  $NVT$  ensemble implies the transfer from single fixed reciprocal temperature  $\beta$  to a set of  $\{\beta_m\}$  (2). Modification means including of factors  $\exp(\eta_m)$ . Each canonical ensemble with the index ( $m$ ) becomes now a subensemble of the expanded ensemble (4).

It is possible to organize a MC random walk in the ensemble (4) in accordance with conventional Metropolis algorithm.<sup>8</sup> Two types of MC steps could occur: (1) usual displacements of particles at fixed temperature and (2) changes of reciprocal temperature with fixed positions of particles. In the second case transition takes place with the probability  $\min\{1, \exp[(\beta_k - \beta_m)H\{x_1\} + \eta_m - \eta_k]\}$ .

In the course of the MC procedure we calculate (for each "m")  $n_m$ —the numbers of MC steps for which the

temperature holds equal to  $1/\beta_m$ . As a result the estimation of the probability for the state with this temperature is obtained:  $p_m \sim n_m/n$  ( $n$ —total length of the MC chain). On the other hand with the account of (3), (4) we have

$$p_m = Z_m \exp(\eta_m) / Z$$

and hence

$$\begin{aligned} \frac{p_m}{p_k} &= \frac{Z_m}{Z_k} \exp(\eta_m - \eta_k) \\ &= \exp(-\beta_m F_m + \beta_k F_k + \eta_m - \eta_k). \end{aligned} \quad (5)$$

Thus we can obtain difference of free energies for any arbitrary pair of temperatures. The case  $\beta_0 = 0$  corresponds to the ideal gas (since the interaction is switched off) and the partition function is known exactly (the case of the hard core will be discussed later). Therefore putting in (5)  $m = 0$ ,  $k = M$  we get

$$\begin{aligned} \beta_M F_M &= -\ln(Z_M) \\ &= -\ln(p_M/p_0) + \eta_M - \eta_0 - \ln(Z_0), \end{aligned} \quad (6)$$

where  $Z_0 = V^N/N!$ —the partition function of the ideal gas.

Since for each fixed  $\beta_m$  we simulate distribution in an ordinary canonical ensemble, averaging over states with  $\beta_m = \text{const}$  yields conventional canonical properties: internal energy, correlation functions, etc. (for the given  $\beta_m$ ). So it is possible to get temperature dependences of these quantities parallel to the free energy calculations in a single MC run.

### B. Choice of parameters $\eta_m$

In principle, as it follows from general considerations of statistical mechanics, the result of calculation ( $F_m$ ) should not depend on values of  $\eta_m$ . However it is evident that probabilities  $p_m$  strongly (exponentially) depend on  $\eta_m$  and hence in the case of inadequate choice of  $\eta_m$  the system will not visit most of the temperature points during a finite MC run at all (e.g., if all  $\eta_m = 0$  the system would almost exclusively occupy the states with the lowest temperature). It is clear that for obtaining good results the probabilities  $p_m$  should be of the same order of magnitude (in any case their variation should not exceed 2–3 orders). The ideal case  $p_m = \text{const} = 1/(M+1)$  corresponds to

$$\eta_m = \beta_m F_m. \quad (7)$$

However,  $F_m$  are just the values to be determined, so the optimal values of  $\eta_m$  are initially unknown [it should be noted that Eqs. (7) do not exactly correspond to the condition of minimum dispersion, though it is clear that deviations from Eqs. (7) would not be large; this problem requires separate investigation].

For the determination of optimal  $\eta_m$  [corresponding to Eq. (7)] one has to make some trial MC runs with relatively small ( $10^4$ – $10^5$ ) number of steps. After initial (as a rule unsuccessful) choice of  $\eta_m$  the system can mainly occupy a single temperature point with rare visits to the neighboring  $\beta_m$ . However even such a short MC run would provide a rough estimation of  $F_m$  for this narrow temperature range and we can use them for optimization of  $\eta_m$  in this region.

The next trial run gives a wider range of  $\beta_m$  with nonzero  $p_m$ . The procedure could be easily optimized and made automatic. An example of such fitting of  $\eta_m$  is presented in the next section. Simulation practice showed that a good set of  $\eta_m$  (when the system repeatedly visits all temperature points during the run of  $\sim 10^5$  MC steps) are obtained already after 2–3 preliminary MC runs even for a strongly nonideal system.

### C. Hard core in the potential

In the specific case of the hard core (e.g., for PRM-electrolyte) the suggested algorithm yields difference of the free energy at given  $\beta$  and at  $\beta = 0$  (hard spheres) for which the exact value of  $F$  is unknown. However the case of the hard core can be readily included in the suggested scheme: one should attribute index “ $m$ ” to the Hamiltonian itself in Eq. (3). The aim is to remove completely (in the limit  $m \rightarrow 0$ ) the hard core in the potential. It could be achieved in several ways, for instance, decreasing the size of the particles or making them penetrable. Thus for the hard charged spheres (RPM electrolyte) one could assume

$$\begin{array}{l} M_0 < m < M \\ m = M_0 \\ 0 \leq m < M_0 \end{array} \left\{ \begin{array}{ll} \pm \beta_m / |r_1 - r_k| & |r_1 - r_k| > d \\ \infty & |r_1 - r_k| < d \\ 0 & |r_1 - r_k| > d \\ \infty & |r_1 - r_k| < d \\ 0 & |r_1 - r_k| > d \\ E_m & |r_1 - r_k| < d \end{array} \right. \begin{array}{l} \text{(RPM)} \\ \text{(hard spheres)} \\ \text{(penetrable spheres).} \end{array} \quad (8)$$

$E_{M_0-1} > \dots > E_0 = 0$  ( $m = 0$  corresponds to the ideal gas).

## III. RESULTS FOR THE RPM ELECTROLYTE

The method was tested on a well-known model—RPM electrolyte in order to compare free energy results with those obtained earlier<sup>4,9-12</sup> with the aid of other methods. The usual scheme was applied: MC periodic cubic cell with equal number ( $N/2$ ) of positive ( $Q = 1$ ) and negative ( $Q = -1$ ) charged hard spheres of diameters  $d$  [interaction potential (8)] and minimum image convention to account for interactions (Ewald summation can be readily included if necessary). Transition attempts with displacement of particles and with the change of “ $m$ ” were made with probability 0.9 and 0.1 correspondingly.

Simulation results for various  $N$  ( $N = 32, 64, 128, 200$ ) at constant density (the side of the MC cube  $L$  varied accordingly) is presented in Table I. Since the values of the free energy for this case are known from the previous papers the values of  $\eta_m$  were initially chosen close to optimal ones (only for  $N = 200$  they were corrected once). An example of MC-walk in the  $\beta$ -space (a piece of MC run  $\sim 1000$  MC steps; Fig. 1) shows that even during this short interval the system walked several times between the extreme points, i.e., from the minimum temperature to the ideal gas and back.

TABLE I. Simulation results in  $\beta$ -expanded canonical ensemble for RPM electrolyte with different  $N$  at constant specific volume  $V/Nd^3 = 104.3$ ;  $\beta = 1$ ,  $d = 0.595$ —in Bjerrum units; (for  $T = 298$  K,  $\epsilon = 78$  it corresponds to ion diam 4.2 Å and ionic strength 0.1038 M).  $F_0$ —free energy of the ideal gas.  $L = V^{1/3}$ —side of the MC cell. Statistical error is shown under corresponding values.

$\beta_m$	$N = 32$ $L = 8.892$ 10 <sup>6</sup> MC steps				$N = 64$ $L = 11.202$ 10 <sup>6</sup> MC steps				$N = 128$ $L = 14.114$ 5 × 10 <sup>5</sup> MC steps			$N = 200^*$ $L = 16.378$ 3 × 10 <sup>5</sup> MC steps	
	$\eta_m/N$	$p_m$	$(F_0 - F_m)/N$	$-U_m/N$	$p_m$	$(F_0 - F_m)/N$	$-U_m/N$	$p_m$	$(F_0 - F_m)/N$	$-U_m/N$	$(F_0 - F_m)/N$	$-U_m/N$	
1.	0.0	0.1605 0.003	0.1997 0.001	0.2819	0.1499 0.005	0.1875 0.001	0.2715	0.0368 0.005	0.1773 0.002	0.269 ...	0.1731 0.001	0.2656	
0.8	0.05	0.1416	0.1823	0.2587	0.1254	0.1684	0.2535	...	...	...	0.1512	0.2477	
0.6	0.1	0.1446	0.1608	0.2363	0.1333	0.1428	0.2315	...	...	...	0.1214	0.2091	
0.4	0.14	0.125	0.1298	0.2089	0.109	0.1065	0.1972	...	...	...	0.0839	0.1792	
0.2	0.18	0.1362	0.073	0.1745	0.0657	0.033	0.1620	...	...	...	0.0029	0.1528	
0.0	0.21	0.1303	-0.0168 <sup>b</sup>	0.0	0.0836	-0.0189 <sup>b</sup>	0.0	0.2065	-0.0203	0.0	-0.0229 <sup>b</sup>	0.0	
(H.S)													
0.0	0.20	0.1619	0.0	0.0	0.3331	0.0	0.0	0.7569	0.0	0.0	0.0	0.0	
(i.g)		0.005			0.01			0.01					
ratio of successful attempts to change $m$			0.63			0.52			0.05			0.42	

\*  $\beta$  interval equals to 0.1.

<sup>b</sup> Shown is  $\beta(F_0 - F)/N$ .

For  $N = 128$  we used no intermediate  $\beta$ -points in the interval  $[0,1]$ . Though in this case the acceptance probability of  $\beta$  transitions decreased, the total computational error practically did not change since the number of “boxes” corresponding to separate canonical subensembles became smaller. However for a still greater number of particles ( $N = 200$ ) the absence of intermediate points decreased the acceptance ratio below 1%. Data for  $N = 200$  in Table I were obtained in a procedure with 10 intermediate points in  $\beta$  interval  $[0,1]$ ; two points with penetrable spheres were added.

Two interconnected factors influence (in opposite directions) the estimation accuracy for  $p_0$  and  $p_M$ : (1) the ratio of successful  $\beta$  transitions and (2) the number of intermediate  $\beta$  points (number of  $\beta_m$  “boxes”). So the optimal acceptance ratio for  $\beta$  transitions (yielding minimum dispersion) could be less than the value of 50%–60% used for configurational steps.

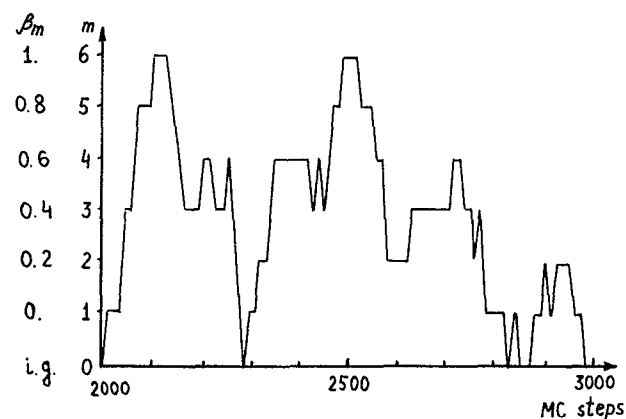


FIG. 1. A pattern of a random walk in the space of  $\{\beta_m\}$  for RPM electrolyte.  $N = 32$ , other parameters—see Table I.

Data of Table I show certain  $N$  dependence of the results. The ultimate values for the macrosystem could be obtained in a usual way by  $1/N$ -extrapolation (they are given in Table III).

Analogous results for a denser system ( $V/Nd^3 = 5.5$  or electrolyte concentration 1.96 M) are presented in Table II.

TABLE II. Results of simulation in  $\beta$ -expanded ensemble for RPM electrolyte.  $\beta = 1$ ,  $d = 0.595$  (Bjerrum units),  $N = 64$ ,  $V/Nd^3 = 5.5$  (1.966 M).  $F_0$ —free energy of the ideal gas. Statistical error is shown under corresponding values.

$\beta_m$	$\eta_m/N$	$p_m$	$\beta(F_0 - F_m)/N$	$-\beta U_m/N$	% Successful $\beta$ transitions
		RPM			
1.	0.0	0.0267 0.005	0.1037 0.006	0.642	44
0.8	0.13	0.0336	-0.0227	0.4757	38
0.6	0.25	0.0361	-0.1416	0.3438	32
0.4	0.37	0.0533	-0.2555	0.2107	30
0.2	0.48	0.1109	-0.354	0.0907	20
0.0	0.58	0.4206	-0.4332	0.0	2.8
(H.S)					
		Penetrable spheres			
3.	0.53	0.1092	-0.4043	-0.0735	8.4
1.5	0.43	0.0551	-0.315	-0.1609	19
0.8	0.33	0.0514	-0.215	-0.1537	24
0.4	0.23	0.0274	-0.1259	-0.1006	17
0.0	0.12	0.0758 0.01	0.0	0.0	
(i.g)					

TABLE III. Comparison of results for RPM electrolyte obtained by different methods ( $\beta = 1$ ).

$\beta(F - F(\text{H.S.}))/N$	$c = 0.1038 \text{ M}$ (see Table I)	$c = 1.96 \text{ M}$ (see Table II)
Present method	$-0.1915 \pm 0.0010$	$-0.5369 \pm 0.0040$
Multistage sampling (Ref. 4)	$-0.1922 \pm 0.0022$	$-0.5236 \pm 0.0045$
HNC (Ref. 9)	$-0.195$	$-0.52$
MEX (Ref. 10)	$-0.1927$	$-0.5165$
$\beta U/N$		
Present method	$-0.271$	$-0.642$
Conventional MC (Ref. 11)	$-0.2739$	$-0.6511$

In this case the problem of transition from hard spheres to the ideal gas already becomes important and we included four intermediate points with penetrable spheres. Nevertheless transitions between hard and penetrable spheres occurred with small probability. It is possible that for denser systems one should provide a more smooth [than according to Eq. (8)] switching off the potential, for instance in the form of a cone with decreasing height:  $E_m(d - |r_1 - r_k|)$  for  $|r_1 - r_k| < d$ .

In Table III comparison of our results with the multistage sampling data<sup>4</sup> and analytical [HNC (Ref. 9) and mode expansion (Ref. 10)] theories is made (compared is

the free energy difference between RPM and hard spheres). Good coincidence is observed. Data for the internal energy is also presented. Agreement with recent results obtained by umbrella sampling<sup>12</sup> is also achieved.

The main advantage of our approach possibly is its applicability to strongly nonideal systems such as RPM at rather low temperatures (see Table IV and Fig. 2). Table IV also illustrates the process of fitting the parameters  $\eta_m$ . It is important to stress that after adequate choice of  $\eta_m$  (after three comparatively short trial runs) the system visited all the temperature points already during a piece of MC chain ( $\sim 10^5$  MC steps), the free energy is determined with high accuracy  $\sim 2\%$  though the statistical error for  $p_m$  could be  $\sim 20\%$ . Actually, the main contributions to the free energies are determined by constants  $\eta_m$ , and the data obtained in further simulation only "corrects" them [the term  $\ln(p_M/p_0)$  in Eq. (6)].

#### IV. GENERALIZATION ON OTHER ENSEMBLES AND DISCUSSION

The general idea of the proposed method can be displayed in the following way. Standard MC simulation in any specific ensemble does not enable one to determine the corresponding complete partition function but makes it possible to calculate the ratio of partition functions for any pair of its subensembles. Really, the partition function of the suben-

TABLE IV. Fitting of  $\eta_m$  for a strongly nonideal system (RPM for  $\beta = 20.$ );  $d = 1.$ ,  $V/Nd^3 = 9.85$ ,  $N = 52$ . 1–3 preliminary runs.

Run		1		2		3		4 (final)			
MC steps		50 000	50 000	50 000	100 000	100 000	100 000	1 000 000			
$\beta_m$	$\eta_m/N$	$p_m$	$\eta_m/N$	$p_m$	$\eta_m/N$	$p_m$	$\eta_m/N$	$p_m$	$-\beta F/N$	$-F/N$	$-E/N$
20.	0.	0.9944	0.	0	0.	0	0.	0.0052 (0.001)	9.557 (0.007)	0.4778	0.5880
19.	0.5	0.0055	0.6	0	0.6	0	0.6	0.0097	8.969	0.4720	0.5811
18.	1.	0.0001	1.2	0	1.2	0	1.2	0.0210	8.383	0.4657	0.5760
17.	1.5	0	1.8	0	1.8	0	1.79	0.0350	7.803	0.4590	0.5715
16.	2.0	0	2.39	0	2.39	0	2.37	0.0498	7.230	0.4519	0.5652
15.	2.45	0	2.97	0	2.97	0	2.93	0.0336	6.663	0.4442	0.5583
14.	2.9	0	3.54	0	3.54	0	3.49	0.0324	6.102	0.4358	0.5516
13.	3.35	0	4.1	0	4.1	0	4.04	0.0334	5.552	0.4271	0.5425
12.	3.8	0	4.65	0	4.65	0.0001	4.58	0.0308	5.011	0.4176	0.5363
11.	4.2	0	5.19	0	5.19	0.0005	5.11	0.0263	4.478	0.4071	0.5274
10.	4.6	0	5.72	0	5.72	0.0010	5.63	0.0258	3.957	0.3957	0.5141
9.	5.	0	6.24	0	6.23	0.0030	6.14	0.0290	3.450	0.3833	0.5008
8.	5.4	0	6.75	0	6.73	0.0036	6.63	0.0199	2.952	0.3690	0.4870
7.	5.75	0	7.25	0	7.21	0.0066	7.12	0.0259	2.467	0.3525	0.4758
6.	6.1	0	7.74	0.0003	7.69	0.0217	7.59	0.0289	1.999	0.3333	0.4588
5.	6.45	0	8.22	0.0028	8.13	0.0302	8.04	0.0301	1.550	0.3101	0.4381
4.	6.7	0	8.69	0.0075	8.57	0.0691	8.48	0.0508	1.123	0.2806	0.4212
3.	7.	0	9.05	0.1015	8.95	0.0569	8.88	0.0414	0.716	0.2388	0.3937
2.	7.3	0	9.55	0.4312	9.27	0.0154	9.23	0.0136	0.345	0.1725	0.3538
1.	7.55	0	9.9	0.2121	9.61	0.0153	9.57	0.0230	0.015	0.0152	0.3023
0.	7.7	0	10.2	0.2042	9.85	0.0116	9.82	0.0403	-0.224	...	0.0
$E_m$		Penetrable spheres									
0.8	...	...	...	...	9.79	0.0753	9.74	0.1533	-0.118	...	-0.0788
0.2	...	...	...	...	9.75	0.1599	9.66	0.1513	-0.039	...	-0.0340
0.	7.5	0	10.	0.0461	9.69	0.5303	9.61	0.0836 (0.01)	0.0	...	0.0

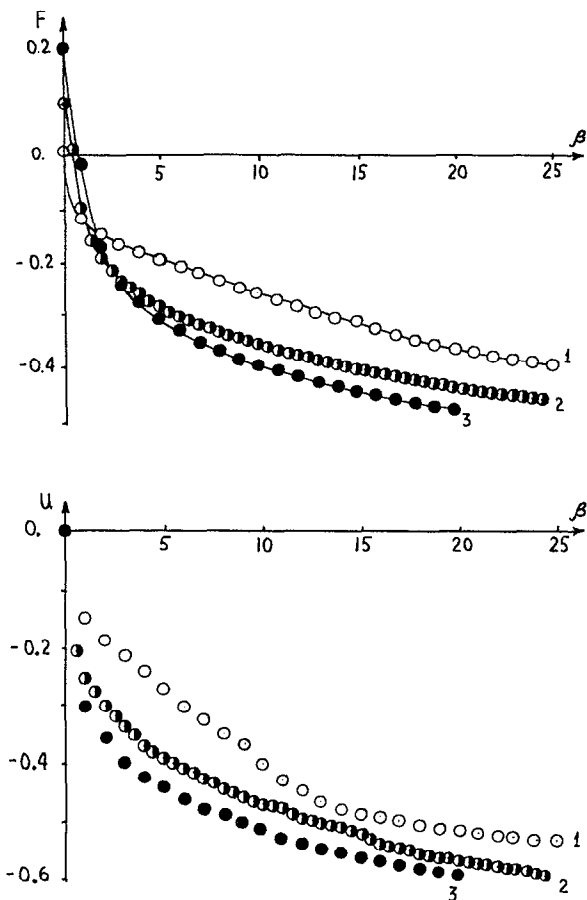


FIG. 2. Free energy (a) and internal energy (b) for RPM electrolyte obtained in expanded ensemble MC simulations.  $d = 1$ , specific volume  $v = V/Nd^3$  and number of particles  $N$ : 1— $v = 99.4$ ,  $N = 50$ ; 2— $v = 20$ ,  $N = 50$ ; 3— $v = 9.85$ ,  $N = 52$ .

semble is proportional to the probability for the system to occur in this subensemble [see Eq. (5)]. It shows the way to direct determination of the partition function, say, for canonical ensemble: to incorporate it as a subensemble into another, expanded, ensemble. The latter should include also exactly determined canonical partition function (reference system—e.g., the ideal gas). Additional factors  $\exp(\eta_m)$  (modification) enable to equalize approximately probabilities for the simulated system to occur in these subensembles thus making calculations practically feasible.

A specific case of  $\beta$  expansion of  $NVT$  ensemble was presented in previous sections. As another example we can treat  $\mu VT$  ensemble which includes in a natural way the reference system—the case of  $N = 0$  (or  $N = 1$ ). Constants  $\eta_m$  are connected with the chemical potential:  $\eta_N = \beta\mu N$ . Of course such choice of  $\eta_N$  is very inefficient for our purpose—determination of the free energy: the system would mostly occupy the states with the number of particles close to a certain  $N_0$  corresponding to the input value of  $\mu$  and would not walk over the whole given (limited) interval of  $N$ :  $[0, N]$ . To provide that the system could visit states with all

numbers of particles in  $[0, N]$  with equal probabilities the constants  $\eta_N$  should be chosen from a recurrent condition  $\eta_{n+1} - \eta_n = \beta\mu(n)$  with the special dependence of  $\mu(n)$ . These conditions are analogous to Eq. (7).

So it is possible to formulate another version of expanded-modified canonical ensemble which actually can be treated as a contracted and modified  $\mu VT$ -ensemble with the partition function

$$Z = \sum_{n=0}^N Z_n \exp(\eta_n).$$

Here  $Z_n$  [contrary to Eq. (4)] is the canonical partition function with varied number of particles  $n$  at constant  $\beta$  and  $V$ . Contraction of the grand canonical ensemble denotes summation in the finite range of  $n = 0, \dots, N$  (instead of  $[0, \infty]$ ), and modification—special dependence of  $\mu$  on  $n$ .

This version of our method was also applied to RPM (Table V) for the same set of parameters as in Table I. A conventional  $\mu$ -ensemble algorithm<sup>13</sup> was used with an explicit restriction on  $n$  ( $0 < n < N$ ) and a special dependence  $\mu(n)$ . Close results for  $N = 32$  are obtained: 0.1997(10) for  $\beta^-$  and 0.1975(55) for  $N$ -expanded ensemble.

Comparison of facilities of both variants shows that though random walk in  $n$  requires less computer time for the same number of MC steps than random walk in  $\beta$  (since in the former case the number of particles  $n$  is mostly less than  $N$ ) still dispersion in  $n$ -expansion version appears to be greater even for equal time of both computations. It is caused primarily by the fact that insertion of a particle is a much greater perturbation for the system than the temperature change. However in  $n$ -expansion procedure we get at once the free energy of the system rather than its difference from that of the hard spheres.

A particular case of the contracted  $\mu VT$  ensemble in which the number of particles changed in a single MC run only by 1 (in the interval  $[N, N + 1]$ ), was suggested in Refs. 14 and 15 for determination of the chemical potential of clusters:  $\mu = F(N + 1) - F(N)$ . For the case of dense periodic systems a similar method with gradual switching on an additional particle was also suggested in Ref. 15.

Analogously it is possible to expand (and modify)  $NVT$  ensemble with respect to volume obtaining this way contracted (finite range of volume  $V$ ) and modified (modification of  $P$ )  $NPT$  ensemble.

It is possible, in general, to create any successive set of points in the space of  $(N, V, T)$  and to follow this set from a given initial point to any final point, corresponding to the ideal system, e.g., at  $N = 0, 1; \beta = 0$  or  $V \rightarrow \infty$ . Other combinations with expansion, contraction, and modification of ensembles are also possible. Thus, expansion of the  $NPT$  ensemble with respect to  $T$  or  $N$  can be used for calculation of the Gibbs potential.

Some of such modifications with “contraction” of grand ensembles (stationary and nonstationary methods) were suggested in fact in Refs. 14 and 15 for calculation of the Gibbs free energy and chemical potential both for clusters and for macrosystems (the term “expanded ensemble” was not yet introduced).

The most close to our approach is the method suggested

TABLE V. Simulation results for RPM electrolyte in  $N$ -expanded canonical ensemble. For  $N_{\max} = 32$  (ionic strength 0.1038 M) the parameters correspond to Table I.

$N$	$\eta_N/N$	$N/V$	$p_N$	$\beta(F_0 - F_N)/N$	$-\beta U_N/N$
0	0.0	0.0	0.0278 0.001	0.0	0.0
2	-0.02	0.0028	0.0308	0.1605	0.1488
4	-0.04	0.0057	0.0426	0.1464	0.1601
6	-0.055	0.0085	0.0471	0.1427	0.1782
8	-0.07	0.0114	0.0510	0.1457	0.1889
10	-0.083	0.0142	0.0595	0.1591	0.1992
12	-0.095	0.0171	0.0607	0.1601	0.2132
14	-0.105	0.0199	0.0616	0.1618	0.2222
16	-0.114	0.0228	0.0636	0.1657	0.2298
18	-0.123	0.0256	0.0635	0.1689	0.2394
20	-0.132	0.0284	0.0660	0.1752	0.2445
22	-0.14	0.0313	0.0691	0.1814	0.2537
24	-0.147	0.0341	0.0678	0.1842	0.2618
26	-0.153	0.037	0.0727	0.1902	0.2677
28	-0.158	0.0398	0.0693	0.1923	0.2717
30	-0.163	0.0427	0.0711	0.1941	0.2807
32	-0.168	0.0455	0.0695 0.004	0.1975 0.0055	0.2854

by Bennet in Ref. 5 and called "acceptance ratio method." If we consider an expanded ensemble composed of systems "0" and "1" it follows from the detailed balance principle for transitions  $0 \leftrightarrow 1$ :

$$\frac{P(0)}{P(1)} = \frac{P(1 \rightarrow 0)}{P(0 \rightarrow 1)}.$$

Hence for calculations of  $P(0)/P(1)$  it is possible to carry out MC simulation separately both for systems "0" and "1" and only to calculate the transition probabilities to the neighboring ensemble (in our terms to subensemble of the expanded ensemble). Actual transitions in Ref. 5 are not made, the only thing done in Ref. 5 is averaging the Metropolis function  $\min\{1, \exp(-\Delta(\beta H))\}$  or another function of the same type which directs MC process. However this

approach has the same shortage as the others: averaging of an exponent. The consequence is that the states with maximum contribution occur rarely and the dispersion is great.

Therefore we strongly believe that actual transitions between subensembles should be made. Consider Fig. 3 where energy distributions for different temperatures are presented. Inclusion of appropriate factors  $\exp(\eta_m)$  shifts them all approximately to the same energy region, the best coincidence being achieved for

$$\Delta\langle U \rangle = \Delta(\eta/\beta). \quad (9)$$

However the optimal choice of  $\eta_m$  corresponding to the uniform distribution over subensembles  $p_m$  is achieved under condition (7) which differs from (9) by the entropy contribution. However since  $\Delta F$  makes as a rule the main contribution to  $\Delta U$  (at least it is valid for PRM electrolyte—see Tables I, II, IV and Fig. 2) addition of  $\eta_m/\beta_m = F_m$  shifts the energy distributions practically to the same region on the energy axis and transitions with the change of temperature occur with sufficiently high probability. The proper choice of  $\eta_m$  solves the problem of optimal sampling distribution: for successful free energy calculation the distribution covering all important points of configurational space for the whole set of  $\beta_m$  is necessary. Our method under condition (7) provides such distribution.

In the proposed method the ultimate result for the free energy is expressed as a ratio of values well determined in the MC process: numbers of "hits"  $n_m$  into definite separate "boxes" (subensembles), the number of boxes being not great (ten or so). It allows one, as it is testified by data in Sec. III, to achieve the same level of efficiency in free energy estimation as in MC calculations of conventional canonical averages (e.g., internal energy)—three decimal figures in a MC chain of about one million steps.

Another attractive feature of the expanded ensemble method especially important for strongly nonideal systems is

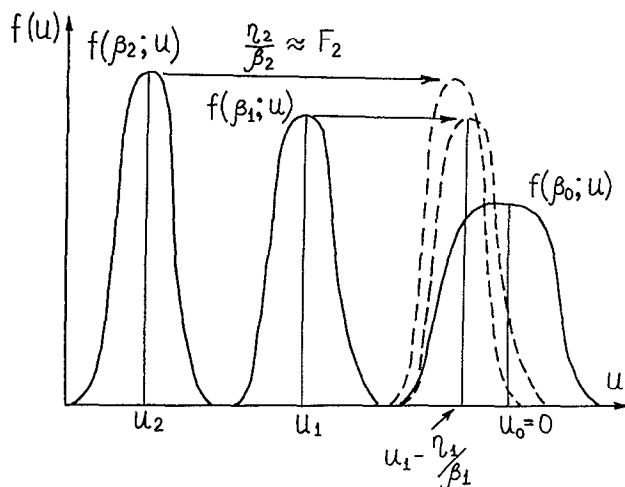


FIG. 3. Schematic diagram of energy distribution shift in  $\beta$ -expanded ensemble.

the increase of “connectivity” of different parts of the configurational space. Actually, in conventional MC simulations at low temperatures there often emerges a problem of metastable states. In the case of an expanded ensemble [let it be  $\beta$  expansion (4)] the system can easily get into the subensemble with higher temperature where the configuration can change drastically in a short time; so after the next decrease of temperature the system may get into the configuration space region far from the initial one, in the vicinity of another minimum. Such a feature of the method could be useful even in MC calculations of conventional canonical averages.

## V. USE OF EXPANDED ENSEMBLES IN PATH INTEGRAL MONTE CARLO PROCEDURE FOR QUANTUM SYSTEMS

The idea of expanded ensembles in free energy calculations can be also developed in quantum statistics. MC simulation in this case is based on Feynman integrals over closed cyclic or (in the case of a system with the permutational symmetry) linked trajectories.<sup>16</sup> Numerical realization implies the use of sublimit approximation of the partition function expressed by a product of high temperature density matrices in coordinate representation:<sup>17-20</sup>

$$\begin{aligned} Y &= \text{Tr}[\exp(-\beta(\hat{K} + \hat{V}))] \\ &= \lim_{J \rightarrow \infty} \text{Tr}[\exp(-\beta\hat{K}/J) \exp(-\beta\hat{V}/J)]^J \\ &\approx \int dQ(1) \cdots dQ(J) \prod_{i=1}^N (y_{m_i}/2\pi\beta\hbar^2)^{3J/2} \\ &\quad \times \exp\left(-\sum_{j=1}^J \sum_{i=1}^N \frac{Jm_i}{2\beta\hbar^2} [q_i(j+1) - q_i(j)]^2\right. \\ &\quad \left.- \frac{\beta}{J} \sum_{j=1}^J V(Q(j))\right) \quad (J \gg 1), \end{aligned} \quad (10)$$

where  $\hat{K}, \hat{V}$ —kinetic and potential energy operators of the  $N$ -particle system of (distinguishable) particles with masses  $m_i$ ,  $Q(j) = [q_i(j), \dots, q_N(j)]$ —a set of “simultaneous” ( $j$ ) vertices of the Feynman trajectories. In terms of Eq. (10) quantum particles are isomorphous with classical cyclic “polymer” chains with  $J$  vertices linked by harmonic forces

$$\gamma_i(j) = \frac{Jm_i}{2\beta^2\hbar^2} [q_i(j+1) - q_i(j)]^2.$$

Interparticle interaction is expressed as interaction of vertices with the same index “ $j$ .” This quantum-classical isomorphism makes it possible to apply here all the above discussed facilities of expanded ensembles.

Contrary to the classical statistics where the mass dependence in the partition function is trivial and hence it is excluded from  $Z$  (3), in the expression (10) for  $Y$  the kinetic part of the partition function is present and includes nontrivial parameters  $m_i$  which yields additional possibilities for creating expanded ensembles.

Consider an expanded ensemble with variable masses of particles  $\tilde{m}_i = \alpha m_i$ , where  $\alpha$  is the parameter with a set of values  $0 < \alpha_1^{-1} < \alpha_2^{-1} < \cdots < \alpha_M^{-1} = 1$ ; in the limit  $\alpha \rightarrow \infty$  the system becomes “classical” with the trajectories in Eq.

(10) collapsing into points. The maximum (finite) value of  $\alpha$  in each specific calculation could be chosen in such a way that  $\lambda_i \ll \bar{r}$  (classical regime) where  $\lambda_i = \hbar/(2\pi\alpha m_i kT)^{1/2}$ —thermal wavelength determining the average size of the corresponding trajectory;  $\bar{r}$ —mean interparticle distance. Suppose that for such a system the partition function and the free energy is determined by the method described in Sec. II. Then

$$-\ln(Y_{\text{CLASS}}) = -\ln(Z) + \sum_{i=1}^N \ln(\lambda_i^3)$$

and the ratio

$$\frac{Y(\alpha_M = 1)}{Y(\alpha_1)} = \frac{Y(\alpha_2)}{Y(\alpha_1)} \frac{Y(\alpha_3)}{Y(\alpha_2)} \cdots \frac{Y(\alpha_M)}{Y(\alpha_{M-1})} \quad (11)$$

with the condition  $Y(\alpha_1) \approx Y_{\text{CLASS}}$  yields contribution to the free energy caused by the quantum effects:

$$-kT \ln[Y(\alpha_M = 1)] - [-kT \ln(Y_{\text{CLASS}})].$$

Calculation of Eq. (11) could be carried out in the same way as in classical statistics with the use of modifying factors  $\exp(\eta_m)$  equalizing statistical sums of the subensembles with different  $\alpha_m$ . It is important to stress that (similar to the classical case) Markov steps from one subensemble to the neighboring ones do not require large calculations: in such a step the trajectory configuration does not change, the change occurs only in the kinetic part of the functional in the exponent (10):

$$\alpha \sum_{j=1}^J \sum_{i=1}^N \gamma_i(j) = \alpha \Gamma\{Q\}.$$

The transition probability matrix can be chosen from the detailed balance condition:

$$\begin{aligned} \frac{P(m \rightarrow m+1)}{P(m+1 \rightarrow m)} &= \exp((\alpha_m - \alpha_{m+1})\beta\Gamma\{Q\}) \\ &\quad \times \exp(\eta_{m+1} - \eta_m), \end{aligned} \quad (12)$$

where  $\eta_m$  have the same meaning as in Eq. (4).

It may seem that the ensemble with fluctuating mass ( $m$ -expanded ensemble) yields nothing new in comparison with the  $\beta$ -expanded ensemble. Actually, calculation of the free energy for quantum systems can be, in principle, carried out also in the ensemble with fluctuating temperature (4),  $\beta = 0$  being chosen as a reference subensemble. However in this case all the route from  $\beta = 0$  up to the given value of  $\beta$  should be passed in the regime of quantum statistical simulation representing each particle by a trajectory while a considerable and may be even the greater part of this route could be passed in the classical simulation regime [Feynman trajectories are strongly localized and can be substituted by classical particles, but the system is nonideal—the potential part in Eq. (10) can not be neglected]. Moreover the separation of quantum effects in the free energy could present an independent interest.

The ensemble with fluctuating mass provides also an alternative approach to another important problem of quantum statistical simulation—the averaging of the kinetic energy operator which (contrary to the potential energy operator) is nondiagonal in the coordinate representation. The problem is the following. The initial kinetic energy estimator

which can be obtained by formal differentiation of free energy on the basis of Eq. (10).

$$\begin{aligned} \langle K \rangle &= - \sum_{i=1}^N \frac{m_i}{\beta} \frac{\partial \ln Y}{\partial m_i} \\ &= \left\langle \frac{3JN}{2\beta} - \frac{J}{2\beta^2 \kappa^2} \sum_{i=1}^N m_i \sum_{j=1}^J [q_i(j+1) - q_i(j)]^2 \right\rangle \end{aligned} \quad (13)$$

is a difference of two values close to each other, the second of which fluctuates with dispersion rising proportionally to  $J$ . So the dispersion of  $\langle K \rangle$  deviates with  $J \rightarrow \infty$  which prevents application of Eq. (13) at low temperatures. The virial estimator of the kinetic energy<sup>19,20</sup> is free from this fault but has another weak point—neglecting of surface contributions. It imposes additional restrictions on the behavior of the wave function [in fact the virial estimator gives correct results for sufficiently bound mixed states lest the potential at the border should be made “soft” and included into  $V(Q)$ ].

On the other hand using the idea of expanded ensembles we can directly calculate the derivative (13) from the profile of  $Y(\alpha m_i)$ . The dispersion of the corresponding ratios (11) determined by transition frequencies  $m \leftrightarrow (m \pm 1)$  could be lowered by optimal choice of factors  $\exp(\eta_m)$ . An important point influencing the decrease of dispersion is determined by the fact that transitions  $m \leftrightarrow (m \pm 1)$  occur without change of trajectory configurations and hence between corresponding points on hypersurfaces  $\exp(-\alpha_m \Gamma\{Q\})$  and  $\exp(-\alpha_{m \pm 1} \Gamma\{Q\})$ . In other words, though  $\Gamma(Q)$  (for  $J \gg 1$ ) can fluctuate during MC process in considerable limits, variations of  $\alpha_m \Gamma\{Q\}$  and  $\alpha_{m \pm 1} \Gamma\{Q\}$  are “synchronized”, thus eliminating great deviations of derivative in Eq. (13). The increase of accuracy can be achieved by the optimal preliminary choice of  $\eta_m$  values corresponding to initial rough estimate of the derivative (13) in the same way as for classical systems (see Sec. II B).

## VI. CONCLUSION

Finally we can suggest some other possible applications of our method.

Calculation of the mean force potentials, e.g., for two ions in water.<sup>21,22</sup> Actually, the potential of mean force  $W(r)$  is the free energy of two ions fixed at an interionic distance  $r$  in water environment at certain temperature. Function  $W(r)$  obtained by expanded ensemble method can be used later for more adequate simulation of electrolyte solution instead of RPM potential.

Another field is the polymer statistics. Calculation of the polymer partition function is also the problem which had not been accurately solved yet: the conventional Metropolis algorithm does not allow to calculate it due to the same reasons as for systems of small particles. Rosenbluth algorithm<sup>23</sup> becomes inefficient for polymer lengths exceeding

several hundred monomers. To solve the problem one can introduce [analogous to Eq. (8)] “penetrable polymer” and construct an expanded–modified ensemble in which the height of potential level  $E$  changes from infinity (self-avoiding polymer) to zero (Gaussian chain). For the latter case the partition function is known exactly to allow one to calculate the partition function of the self-avoiding chain.

Suggested method can be applied also to the study of conformational transitions in the macromolecules caused by the change of environment (e.g., many conformational transitions in proteins, DNA, take place when temperature or salt concentration is changed<sup>7,24</sup>). There are two ways for calculation FED for a pair of its forms. The first is to create an “expanded over conformations” ensemble in which the initial conformation gradually turns into the final one (the intermediate conformations could be chosen nonphysical). If this way is found to be difficult for realization (due to technical reasons, e.g., for complicated macromolecules) the  $\beta$ -expansion variant can be used. Its advantage is that conformation of the macromolecule in this version is fixed.

<sup>1</sup> Z. M. Salsburg, J. D. Jacobson, W. Fickett, and W. W. Wood, *J. Chem. Phys.* **30**, 65 (1959).

<sup>2</sup> G. Ciccoli and W. G. Hoover, *Molecular Dynamics Simulation of Statistical Mechanics Systems*, Proc. of the Int. School of Physics “Enrico Fermi,” Amsterdam-Oxford-N.Y.-Tokyo, 1986.

<sup>3</sup> B. Widom, *J. Chem. Phys.* **39**, 2808 (1963).

<sup>4</sup> J. P. Valleau and D. N. Card, *J. Chem. Phys.* **57**, 5457 (1972).

<sup>5</sup> C. H. Bennett, *J. Comput. Phys.* **22**, 245 (1976).

<sup>6</sup> J. P. Valleau, *J. Comput. Phys.* **23**, 187 (1977).

<sup>7</sup> D. L. Beveridge and F. M. DiCapua, *Annu. Rev. Biophys. Chem.* **18**, 431 (1989).

<sup>8</sup> *Monte Carlo Methods in the Statistical Physics*, edited by K. Binder (Springer, Berlin, Heidelberg, New York, 1979).

<sup>9</sup> J. C. Rasaiah and H. Friedman, *J. Chem. Phys.* **48**, 2742 (1968).

<sup>10</sup> H. C. Andersen and D. Chandler, *J. Chem. Phys.* **55**, 1497 (1971).

<sup>11</sup> J. C. Rasaiah, D. N. Card, and J. P. Valleau, *J. Chem. Phys.* **52**, 6232 (1970).

<sup>12</sup> I. S. Graham and J. P. Valleau, *J. Phys. Chem.* **63**, 7894 (1990).

<sup>13</sup> J. P. Valleau and L. K. Cohen, *J. Chem. Phys.* **72**, 5935 (1980).

<sup>14</sup> S. V. Shevkunov, A. A. Martynovskii, and P. N. Vorontsov-Velyaminov, *High Temp. Phys. (USSR)* **26**, 246 (1988).

<sup>15</sup> S. V. Shevkunov, P. N. Vorontsov-Velyaminov, and A. A. Martynovskii, *Mol. Simul.* **5**, 119 (1990).

<sup>16</sup> R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals*, (McGraw-Hill, New York, 1965).

<sup>17</sup> L. D. Fosdick and H. F. Jordan, *Phys. Rev.* **143**, 58 (1966).

<sup>18</sup> J. A. Barker, *J. Chem. Phys.* **70**, 2914 (1979).

<sup>19</sup> M. F. Herman, E. J. Bruskin, and B. J. Berne, *J. Chem. Phys.* **76**, 5150 (1982).

<sup>20</sup> R. N. Barnett, U. Landman, C. L. Cleveland, and J. Jortner, *J. Chem. Phys.* **88**, 4429 (1988).

<sup>21</sup> I. R. McDonald and J. C. Rasaiah, *Chem. Phys. Lett.* **34**, 382 (1975).

<sup>22</sup> M. Berkowitz, O. A. Karim, J. A. McCammon, and P. J. Rossky, *Chem. Phys. Lett.* **105**, 577 (1984).

<sup>23</sup> M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.* **23**, 356 (1955).

<sup>24</sup> M. D. Frank-Kamenetskii, A. V. Lukashin, and V. V. Anshelevich, *J. Biomol. Struct. Dyn.* **3**, 35 (1985).