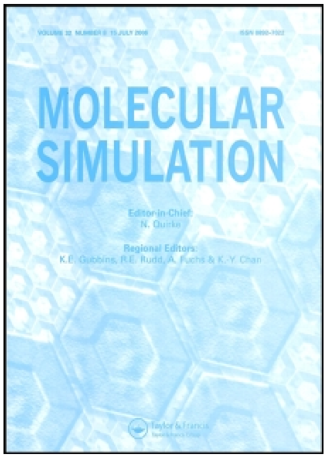

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The Effect of the Combined Volume on the Efficiency of Gibbs Ensemble Simulations

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Note

THE EFFECT OF THE COMBINED VOLUME ON THE EFFICIENCY OF GIBBS ENSEMBLE SIMULATIONS

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INTRODUCTION

Simulation in the Gibbs ensemble, introduced [1,2] and recently reviewed [3] by Panagiotopoulos, combines simulation techniques in the canonical, isobaric and grand-canonical ensembles (all at constant temperature). It has been immediately recognized that the method will face similar limitations at liquid densities as the grand-canonical ensemble simulations, the difficulty of inserting a new molecule into the liquid phase [4]. Accordingly, the cavity biased insertion, originally developed in the grand-canonical ensemble [5,6] was shown to improve the simulation efficiency [7] and improvements in the insertion success rate were also obtained with an orientational biasing technique [8].

THEORY

This note concerns itself with an other difficulty that is due to the very low density of the vapor phase. The problem here is that putting even one molecule into the vapor phase increases the density well above the thermodynamic average and as a result it is very unlikely to see there two or more. However, if the combined volume is chosen high enough so that the thermodynamic average of the vapor density requires more than one molecule in the vapor phase, the density fluctuations can be expected to improve markedly.

CALCULATIONS

This idea was tested on liquid benzene, using the OPLS [9] united atom representation for the =CH− group. The simulations were performed on 300 molecules,

Table 1 Simulation results with different volumes at 300 K. The runlength is in million attempted displacements, CB and R indicate cavity-biased and random insertions, respectively, V_{cmb} is the combined volume in Å^3, ρ_l and ρ_v are the liquid and vapor densities in g/ml, P_{exc} is the probability of acceptance of a molecule exchange attempt, the numbers under Δ_{molec} are the range of fluctuations in the number of molecules cumulatively and for the last 1 million step stretch.

Runlength	V_{cmb}	ρ_l	ρ_v	$<N_v>$	P^{exc}	Δ_{molec}	
1 CB	42875	0.8590 ± 0.0036	0.00197 ± 0.00117	0.62	0.00012	3	3
2 CB	42875	0.8567 ± 0.0032	0.00128 ± 0.00068	0.40	0.00013	3	2
3 CB	42875	0.8584 ± 0.0026	0.00128 ± 0.00049	0.40	0.00012	3	3
4 CB	42875	0.8582 ± 0.0020	0.00108 ± 0.00037	0.34	0.00013	3	2
1 CB	250000	0.8622 ± 0.0026	0.00076 ± 0.00019	1.20	0.00029	5	5
2 CB	250000	0.8571 ± 0.0039	0.00056 ± 0.00017	0.88	0.00036	5	3
3 CB	250000	0.8558 ± 0.0035	0.00049 ± 0.00014	0.78	0.00039	5	4
4 CB	250000	0.8569 ± 0.0029	0.00050 ± 0.00012	0.78	0.00039	5	4
1 CB	823750	0.8522 ± 0.0037	0.00029 ± 0.00009	1.78	0.00083	6	6
2 CB	823750	0.8544 ± 0.0040	0.00039 ± 0.00009	2.39	0.00069	7	7
3 CB	823750	0.8554 ± 0.0037	0.00042 ± 0.00009	2.57	0.00067	7	7
4 CB	823750	0.8558 ± 0.0038	0.00051 ± 0.00010	3.11	0.00059	9	9
1 R	42875	0.8577 ± 0.0027	0.00000 ± 0.00000	0.0	0.0	0	
1 R	250000	0.8566 ± 0.0037	0.00052 ± 0.00019	0.83	.000003	2	
1 R	823750	0.8584 ± 0.0044	0.00011 ± 0.00007	0.67	.000003	2	

using cavity-biased insertions [7] with the cavity radius fluctuating around 4.2 Å. Interaction energies between molecules where the center-to-center distance was larger than 12 Å were set to zero. Molecule exchanges were attempted after every pair of displacement attempts and volume exchanges were attempted after every 100 displacement attempt pairs. Initial calculations used a combined volume of 42857 Å^3 - this choice results in a vapor phase volume commensurable with that of the liquid phase. These calculations also gave an approximate value for the vapor density that was used to derived a new combined volume 250000 Å^3, that provides a large enough vapor phase that the average number of molecules there is more than one and an even larger volume, corresponding to about two molecules in the vapor phase, 823750 Å^3. These volumes correspond to two cubes of edges 35 Å, 50 Å and 75 Å, respectively.

In addition, calculations were also performed without using the cavity-biased insertion technique, in order to assess its relative importance in relation to the technique suggested in this note.

RESULTS AND DISCUSSION

The results of calculations at 300 K temperature (near the benzene's melting point, 280 K [20]) with these three different combined volumes are shown in Table 1. The calculated liquid density compares well with the experimental value, 0.8789 g/ml [20], especially considering the relatively short cutoff used. The benefit from the increased combined volume can be seen in the increased fluctuation in the number of molecules, in the increased acceptance probabilities of the exchange step and last, but not least in the clearly superior convergence of the vapor density, without any apparent loss of precision in the liquid side. Thus these results suggest that the combined volume for a Gibbs ensemble simulation should be large enough to contain at least two molecules, *on the average*.

Calculations without cavity biasing, also summarized in Table 1, show that improvement in the exchange acceptance rates produced by increasing the combined volume and by cavity biasing is additive if not synergistic, supporting the initial reasoning that there are two different effects that reduce the exchange rate below acceptable levels at lower temperatures. While cavity biasing appears to produce more improvement than the volume increase, the computational overhead is about 20% for cavity biasing and none for the increase in the combined volume.

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