MOLECULAR PHYSICS, 1999, Vol. 96, No. 2, 293-296 Taylor & Francis, Ltd.

RESEARCH NOTE

The Anisotropic Virial-Biased Sampling for Monte Carlo Simulations in the Isobaric-Isothermal Ensemble

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Running title: Anisotropic virial-biased Monte Carlo

Abstract

The original virial-biased sampling of Mezei [1] that changes the simulation cell's volume isotropically has been generalized to anisotropical changes. Calculations on liquid water and the aqueous solution of the dimethyl phospate – sodium ion pair demonstrate the computational gains of the virial biased techniqes.

1. **Introduction**

Monte Carlo computer simulation in the isothermal-isobaric (T, P, N) ensemble requires periodic change of the simulation cell. Such steps are computationaly expensive since all intermolecular distances change. It has been shown earlier [1] that replacing the sampling of the volume change from a uniform distribution by a sampling proportional to the virial sum, called virial-biased sampling allows for larger volume changes at each try. This in turn allows the less frequent attempts of volume changes, resulting in significant savings of computational efforts. It has been also noted [2] that simulations in the Gibbs ensemble would also benefit from such biased sampling.

The purpose of this paper is to show that if the volume changes are not performed isotropically than additional computational gain can be achieved if the change of the simulation cell along each direction is biased independently based on the *components* of the virial sum. This advantage will be of particular significance when the simulation cell is inherently anisotropic.

2. **Theory and Background**

One of the versions of the virial-based volume change was designed along the lines of the force-biased sampling of Pangali, Rao and Berne [3]. The role of the force was played by the quantity $F_{\rm v}$:

$$F_{\rm v} = -\frac{\partial U}{\partial V} - p + \frac{kTN}{V} = \sum_{i<j}^{N} \left(\frac{\partial u(\mathbf{r}_{\rm i}, \mathbf{r}_{\rm j})}{\partial \mathbf{r}} \cdot (\mathbf{r}_{\rm i} - \mathbf{r}_{\rm j}) \right) /3V - p + \frac{kTN}{V} \,, \tag{1}$$

where U is the energy of the system, V is the volume of the simulation cell, p is the pressure, N is the number of molecules, T is the absolute temperature and k is the Boltzmann factor. The second equality is valid for pairwise additive potentials $u(\mathbf{r}_{\rm i}, \mathbf{r}_{\rm j})$ where the $\mathbf{r}_{\rm i}$ are the coordinates of the molecular centers — as follows from the expression of pressure in terms of the virial sum. The sampling of the volume change δV is from the distribution

$$P(\delta V) = \frac{\exp(\lambda F_{\rm v} \delta V / kT)}{n(\Delta V, F_{\rm v}, \lambda)} \,, \tag{2}$$

where ΔV is the allowed range for the volume change, λ is a scaling factor whose value was set to $1/2$ (following Ref. 2) and $n(\Delta V, F_{\rm v}, \lambda)$ is the normalization factor:

$$n(\Delta V, F_{\rm v}, \lambda) = \int_{-\Delta V}^{\Delta V} \exp(\lambda F_{\rm v} v / kT) dv = \frac{2kT \sinh(\lambda F_{\rm v} \Delta V / kT)}{\lambda F_{\rm v}} \,. \tag{3}$$

The acceptance probability $P_{\rm acc}$ of a biased step is given as

$$\begin{aligned} P_{\rm acc} = \min\{1, \exp[(U_{\rm o} - U_{\rm n} - P\delta V)/kT + N(\ln V_{\rm n} - \ln V_{\rm o})] * \\ \frac{n(\Delta V, F_{\rm v,o}, \lambda)}{n(\Delta V, F_{\rm v,n}, \lambda)} \exp[-\lambda(F_{\rm v,o} + F_{\rm v,n})\delta V / kT]\} \,, \end{aligned} \tag{4}$$

where the subscripts o and n refer to the configurations before and after the attempted move. Dropping the second and third factors in Eq. (4) reduces it to the acceptance probability of an unbiased step.

Given a source of random numbers ξ with uniform distribution in the interval $[0, 1]$, the sampling from the above distribution results in volume changes expressed as

$$\delta V = \frac{kT \ln[2\xi \sinh(\lambda F_{\rm v} \Delta V/kT) + \exp(-\lambda F_{\rm v} \Delta V/kT)]}{\lambda F_{\rm v}} \,. \tag{5}$$

The anisotropic virial biasing introduced here samples the changes along the x direction, δx from the distribution

$$P(\delta x) = \frac{\exp(\lambda F_{\rm x} \delta x E_{\rm y} E_{\rm z}/kT)}{n(\Delta V_{\rm x}, F_{\rm x}, \lambda)} \,, \tag{6}$$

where $\Delta V_{\rm x}$ is the range the cell volume is allowed to change in the x direction (during a single move), $E_{\rm y}, E_{\rm z}$ are the simulation cell edges in the y and z directions, respectively, and

$$F_{\rm x} = -\left(\frac{\partial U}{\partial V}\right)_{\rm x} - \frac{p}{3} + \frac{kTN}{3V} \,. \tag{7}$$

Here $\left(\frac{\partial U}{\partial V}\right)_{\rm x}$ is the contribution of the x component to $\frac{\partial U}{\partial V}$. Again, for pairwise additive potentials $u(\mathbf{r}_{\rm i}, \mathbf{r}_{\rm j})$

$$\left(\frac{\partial U}{\partial V}\right)_{\rm x} = \sum_{i<j}^{N} \frac{\partial u(\mathbf{r}_{\rm i}, \mathbf{r}_{\rm j})}{\partial \mathbf{r}_{\rm i_x}} (\mathbf{r}_{\rm i} - \mathbf{r}_{\rm j})_{\rm x}/3V \,. \tag{8}$$

Similar expressions hold for the y and z directions. When the cell dimensions are changed independently in a biased manner, then $P(\Delta V)$ is replaced by $P(\Delta V_{\rm x})\, P(\Delta V_{\rm y})\, P(\Delta V_{\rm x})$. Thus, in Eq. (4) $F_{\rm v}$ and $n(\Delta V, F_{\rm v}, \lambda)$ should be replaced by the corresponding products to yield the acceptance probability $P_{\rm acc}$:

$$P_{\rm acc} = \min\{1, \exp[(U_{\rm o} - U_{\rm n} - P\delta V)/kT + N(\ln V_{\rm n} - \ln V_{\rm o})] *$$
$$\exp[-\lambda[(F_{\rm x,o} + F_{\rm x,n})\delta x E_{\rm y} E_{\rm z} + (F_{\rm y,o} + F_{\rm y,n})\delta y E_{\rm x} E_{\rm z} + (F_{\rm z,o} + F_{\rm z,n})\delta z E_{\rm x} E_{\rm y}]/kT]\} *$$

$$\frac{n(\Delta V_{\rm x}, F_{\rm x,o}, \lambda))n(\Delta V_{\rm y}, F_{\rm y,o}, \lambda)n(\Delta V_{\rm z}, F_{\rm z,o}, \lambda)}{n(\Delta V_{\rm x}, F_{\rm x,n}, \lambda)n(\Delta V_{\rm y}, F_{\rm y,n}, \lambda)n(\Delta V_{\rm z}, F_{\rm z,n}, \lambda)} \,. \tag{9}$$

Since the anisotropic sampling described here changes the shape of the cell there are certain limitations in its application depending on the choice of the periodic cell. Cells based on hexagonal or face-centered cubic close packing require fixed ratios of edges, completely excluding anisotropic sampling. Prism-shaped cells (like hexagonal or triangular prisms) allow

only partially anisotriopic sampling: changes along the two axes perpendicular to the prism axis have to be correlated. Rectangular cells allow any edge ratio.

For partially anisotropic sampling (assuming that the prism axis is along the x direction) the volume change involves a change δx along the x direction and a change of area δyz in the prism's cross section using biasing forces $F_{\rm x}$ and $F_{\rm yz}$, respectively with

$$F_{\rm yz} = F_{\rm y} + F_{\rm z}\,. \tag{10}$$

The probability of selecting δyz is given by replacing δx, $F_{\rm x}$ and $\Delta V_{\rm x}$ in Eq. (6) by δyz, $F_{\rm xy}$ and $\Delta V_{\rm yz}$, respectively ($\Delta V_{\rm yz}$ being the allowed range of volume change due to the change of area in the xy plane).

It should be stressed that any version of the virial-biased sampling requires the calculation of the forces on the molecules — a calculation not normally required during Monte Carlo simulations, adding about 30% to the computational burden. However, if the molecular displacement steps are done using the force-biased sampling [3], then the forces are already available for virial biasing.

3. **Calculations and Results**

We have compared the efficiency of the new anisotropic virial biased method with that of the ordinary unbiased isothermal-isobaric Monte Carlo method [4] as well as with the isotropic virial bias technique [1] in room-temperature aqueous systems. For the comparison of the efficiency of the various sampling techniques the average magnitude of the accepted volume changes $\delta V_{\rm acc}$ seems to be an appropriate quantity. However, it is an adequate indicator of the sampling efficiency of only those techniques in which the sign of the volume change (i.e., whether the system is expanding or contracting) is correlated along the three axes of the simulation box. In the case of the anisotropic virial-biased sampling the cell may expand along one axis and shrink along an other one in the same volume change step, which makes the quantity $\delta V_{\rm acc}$ an inadequate measure of the sampling efficiency in this case. Therefore we have calculated the quantity $\delta XYZ_{\rm acc}$:

$$\delta XYZ_{\rm acc} = |(\delta x)E_{\rm y}E_{\rm z}| + |(\delta y)E_{\rm x}E_{\rm z}| + |(\delta z)E_{\rm x}E_{\rm y}|\,. \tag{11}$$

It should be noted that for correlated changes of the cell size along the three axes in the limit of small steps $\delta XYZ_{\rm acc}$ agrees with $\delta V_{\rm acc}$.

We have compared the efficiency of the different sampling methods in three different systems. Both systems I and II have contained 512 water molecules. The initial simulation box was cubic in system I with edge length 26.0 $\mathring{A}$, whereas in system II it was rectangular with $E_{\rm x}$=40.0 $\mathring{A}$, and $E_{\rm y} = E_{\rm z}$=20.0 $\mathring{A}$ at the beginning of the simulation. System III was a dilute aqueous solution of dimethylphosphate-sodium, containing one $(CH_3)_2PO_2^-$ Na^+ ion pair and 512 water molecules in the same initial rectangular box as system II. The ion pair has then been kept fixed in the entire simulation. Water-water interactions have been described by the TIP4P model [5] whereas the parameters of the ion-water interactions have been taken from the AMBER library [6].

The three systems have been equilibrated by 12 million particle displacement steps using force biased sampling [3]. The maximum translation of the water molecules and their maximum rotation around a randomly selected space-fixed axis in one particle displacement step have been set to 0.275 $\mathring{A}$ and 20^{o}, respectively. The obtained rate of acceptance of these steps was about 0.5. Every 200 particle displacement step was followed by a volume change trial. During the equilibration period no biasing was employed in these steps. After the equilibration process was finished two separate simulations have been performed on each system with all the three sampling methods (i.e., unbiased, isotropic virial biased, anisotropic virial biased). In run A the cell size have been changed along all the three axes simultaneously in each volume change step, whereas in run B it has only been altered along one of the axes in one step. In every simulation run 5 million force biased particle displacement steps have been performed, every 200 of them being followed by a volume change step. The stepsize parameters (ΔV, ΔV_{x}, ΔV_{y}, ΔV_{z}) have been tuned to yield about a 25% acceptance rate for the volume change steps. (The obtained rates of acceptance have been between 23.5% and 27.0% in every simulation). In this way the efficiency of the different sampling methods can be compared directly through the resulting $\delta XYZ_{\mathrm{acc}}$ values. The energy and density of the systems were found to be unaffected by the employed sampling method and agreed with each other within the error limits of their calculation.

Table 1. Average cell edges and sampling efficiencies $\langle \delta XYZ_{\mathrm{acc}} \rangle / \mathring{A}^3$ as obtained from simulations with different sampling methods with a volume change acceptance rate of about 25%. Systems I, II and III are waters in a cubic box, waters in a prism-like box and aqueous solutin of dimethyl phosphate-sodium in a prism-like box, respectively. For further details, see text.)

	RUN A			RUN B		
	unbiased	isotropic virial bias	anisotropic virial bias	unbiased	isotropic virial bias	anisotropic virial bias
Sytem I	73.38	112.83	167.81	55.69	71.37	68.59
Sytem II	61.28	87.95	115.21	47.76	62.89	57.86
System III	59.83	88.86	114.01	48.61	61.37	58.37

The obtained $\delta XYZ_{\mathrm{acc}}$ values as well as the average lengths and standard deviations of the three edges of the simulation box are summarised in Tables 1, 2 and 3 as obtained from the different simulations of systems I, II, and III, respectively. As is evident from the resulting data, the anisotropic virial biased method proved to be the most efficient one in the A type runs, i.e., when the cellsize was altered in all three dimensions simultaneously in each volume change steps. The resulting $\delta XYZ_{\mathrm{acc}}$ value is about 130% and 50% higher as obtained with the new method than with uniform and isotropic virial biased sampling, respectively, in the case of system I. These values are about 90% and 30% for systems II and III, i.e., those having long rectangular simulation box. This difference in the computational gain obtained with the new anisotropic virial biased sampling method between systems having simulation boxes of different shape can be explained with the fact that a given volume change requires larger change of the intermolecular distances along the longest edge of the rectangular simulation

box than along any direction in a cubic one, and this involves larger changes in the energetics of the system. This is also the reason why run A always results in larger $\delta XYZ_{\rm acc}$ values than run B. Namely, the change of the intermolecular distances along the changing axis for a given volume change in a B type run is about three times large as the same distance change in an A type run. There is, of course, no reason for using B type volume changing steps in the simulation of isotropic systems. On the other hand, when the simulated system is highly anisotropic (e.g., interfaces, liquid crystals, surfactant solutions, lipid membranes, etc.) the use of this kind of volume changing steps could be mandatory for obtaining reliable results (since the aspect ratio of such systems may not be know in advance).

When comparing the efficiency of the three sampling techniques for B type runs the resulting picture is somewhat different from the case of A type runs. Here the efficiency of the isotropic and anisotropic virial biased methods are roughly equivalent, the isotropic method being slightly (about 4-8%) better than the anisotropic one whereas again both methods result in considerably larger (20-30%) $\delta XYZ_{\rm acc}$ values than the unbiased sampling. The reason of the relatively small computational gain of virial biasing (compared to the A-type runs) again lies in the fact that due to the required relatively large changes of the intermolecular distances the largest possible volume changes are relatively small in each step and this limits the possible increase of $\delta V_{\rm acc}$ obtainable by any kind of sampling.

It is surprising that the isotropic virial biased method results in better sampling efficiency for B type runs than the anisotropic one, although this difference is rather small. The reason of this could be that the anisotropic method can largely distort the shape of the simulation box (as can also be seen from the resulting mean values and fluctuations of the cell edges, see Tables 1-3), which can then lead to a slight increase of the sampling efficiency. In order to investigate this point further we have repeated the virial biased B type runs for all the three systems with smaller stepsize parameters yielding an about 50% rate of accepted and tried volume change steps instead of 25%. The results of these runs are summarised in Table 4. As demonstrated, the relative efficiency of the two virial biased methods is now reversed: the anisotropic method is slightly (by about 4%) more efficient for systems I and II and almost the same for system II. These findings suggest that there is no important difference between the efficiency of the two virial biased sampling methods in B type runs.

Summarising, the new anisotropic virial biased isothermal-isobaric Monte Carlo method provides a great improvement in the volume sampling efficiency for isotropic systems, when volume changes can be performed simultaneously along all the three axes of the simulation box. For anisotropic systems when the volume can only be changed along one axis in one step the sampling efficiency of the new method does not differ largely from that of the isotropic virial biased technique but it is still considerably better than the performance of the unbiased sampling.

Acknowledgement

P. J. is grateful to the Soros Foundation, Budapest, for its financial support.

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