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Note

Computational Techniques for Spherical Boundary Conditions

I. Introduction

In a previous paper [1], spherical boundary conditions (SBC) for computer simulation of thermodynamic systems were introduced. The D-dimensional system (volume V) lies on the surface of a $(D+1)$-dimensional sphere with radius R. This sphere is centered at the origin and will be called Σ in the following. To generate random moves for Monte Carlo, a further sphere Δ (radius δ) will be introduced. The center of Δ coincides with the center of the particle to be moved in a given Monte Carlo step and thus lies on the surface of Σ. The spheres Σ and Δ are imbedded in $(D+1)$-dimensional Euclidean space, whereas noneuclidean geometry has to be used as to the D-dimensional system. The particles lie totally on the surface of Σ, e.g., disks becoming calottes. All distances within the system are geodesic ones, i.e., segments of great circles.

As in [1], the canonical (NVT) ensemble is considered. Periodical boundary conditions (PBC) and SBC differ in the method generating the configurations (see Sections II and III). Given these configurations, the thermodynamic quantities are determined for SBC and PBC in a similar way.

The first suggestion of SBC [2] was originally unknown to us. Parallel to our theoretical approach [1], another group independently obtained molecular dynamics data for two-dimensional SBC [3, 4] studying long-range potentials. Packings of hard disks and spheres have also been obtained by the use of SBC [5, 6].

II. Monte Carlo with SBC

For computational reasons, it is most convenient to set $R = 1$, Σ being a unit sphere. In the following equations, however, R will be included for the sake of clarity.

A sample of N equal D-dimensional particles is placed on the surface of the $(D+1)$-dimensional sphere Σ (radius R) centered at the origin. The position of molecule i is defined by a vector $\mathbf{r}_i$ with Cartesian coordinates satisfying the condition

$$2D: \quad x_i^2 + y_i^2 + z_i^2 = R^2, \tag{1a}$$

$$3D: \quad x_i^2 + y_i^2 + z_i^2 + w_i^2 = R^2. \tag{1b}$$

The distance r_{ij} between two particles is the shortest connection *within space*, i.e., the

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length of the smaller segment of the connecting great circle. It is easily calculated by taking the scalar product of position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$:

$$2D: \qquad r_{ij}/R = \cos^{-1}[(x_i x_j + y_i y_j + z_i z_j)/R^2], \tag{2a}$$

$$3D: \qquad r_{ij}/R = \cos^{-1}[(x_i x_j + y_i y_j + z_i z_j + w_i w_j)/R^2]. \tag{2b}$$

The simple structure of these equations was one of the main arguments to use Cartesian instead of polar coordinates. For example, (2a) turns into

$$r_{ij}/R = \cos^{-1}[\cos\theta_i \cos\theta_j + \sin\theta_i \sin\theta_j \cos(\varphi_i - \varphi_j)] \tag{3}$$

using polar coordinates, θ_k and φ_k being defined as usual. Although one wastes storage for N coordinates with Cartesian formulation, higher speed in evaluating distances will make up for that by far.

Now we turn to the generation of random moves necessary for Monte Carlo simulation [7]. Let p_{kn} denote the single step probability from state k to state n (with energy E_n) to occur. Then the following relation must be satisfied [7]:

$$u_k p_{kn} = u_n p_{nk}, \qquad u_n = \exp(-E_n/kT). \tag{4}$$

Now suppose configurations k and n differ only by a random move of one particle, say m. Then p_{kn} may be factorized:

$$p_{kn} = p_{kn}^{\text{trial}} \times p_{kn}^{\text{accept}} = p_{kn}^{\text{trial}} \times \min[1, \exp(E_k - E_n)/kT], \tag{5a}$$

where p_{kn}^{trial} and p_{kn}^{accept} give the respective probabilities for trial and thermodynamic acceptance of the move $k \to n$. p_{kn}^{accept} is usual Monte Carlo. For SBC, however, p_{kn}^{trial} has to be modified. For PBC, $p_{kn}^{\text{trial}} = \text{const}$ within a small D-dimensional cube around the old position of particle m, and zero outside. Generally,

$$p_{kn}^{\text{trial}} = p_{nk}^{\text{trial}} \tag{5b}$$

is the result when combining (4) and (5a). For SBC, this is most easily achieved by isotropic displacements. For $D = 2$, one could choose two random numbers defining distance and angle of the random move. This is very straightforward in principle but awkward to handle on the computer. First one has to transform $\mathbf{r}_m$ to the north pole, generate the random move and transform back. This involves matrix algebra for each move with the possibility of vanishing determinants. Thus we adopted another procedure based on a method due to Marsaglia [8].

For a start, a random point has to be generated on the surface of a $(D+1)$-dimensional sphere Δ (radius δ) mentioned in the introduction. Correspondingly, we label this procedure *surface sampling*. Generally, $\delta \ll R$, thus $\bar{r} = R \sin^{-1}(\delta/R) \approx \delta$, $\bar{r}$ being the maximum displacement of the random move of particle m. Sphere Δ is centered at $\mathbf{r}_m$, the position of m before the trial.

For $D = 2$, we generate two random numbers v_1 and v_2 independent and uniform on $[-1, 1]$ until $S \equiv v_1^2 + v_2^2 < 1$ is fulfilled. Then the vector $\boldsymbol{\delta} = (\delta_x, \delta_y, \delta_z)$,

$$2D: \qquad \delta_x = 2\delta v_1(1-S)^{1/2}, \qquad \delta_y = 2\delta v_2(1-S)^{1/2}, \qquad \delta_z = \delta(1-S), \quad (6a)$$

is uniform on the surface of Δ. For $D = 3$, generate v_1 and v_2 independent uniform on $[-1, 1]$ until $S_1 \equiv v_1^2 + v_2^2 < 1$. Then choose v_3 and v_4 independent and uniform on $[-1, 1]$ until $S_2 \equiv v_3^2 + v_4^2 < 1$ is fulfilled. The resulting vector $\boldsymbol{\delta}$,

$$3D: \quad \delta_x = \delta v_1, \quad \delta_y = \delta v_2, \quad \delta_z = \delta v_3[(1-S_1)/S_2]^{1/2}, \quad \delta_w = \delta v_4[(1-S_1)/S_2]^{1/2}, \quad (6b)$$

is uniform on the surface of Δ. Now add $\boldsymbol{\delta}$ to the current position $\mathbf{r}_m$ and normalize the result to length R. The new position $\mathbf{r}_m^{\text{new}}$ is given by

$$D = 2, 3: \qquad \mathbf{r}_m^{\text{new}} = R(\mathbf{r}_m + \boldsymbol{\delta})|\mathbf{r}_m + \boldsymbol{\delta}|^{-1}, \quad (7)$$

see Fig. 1. The resulting probability density for the displacement is isotropic up to $\bar{r} = R \sin^{-1}(\delta/R) \approx \delta$, and zero for larger displacements. It is, however, by no means uniform, see below. The described method is easy to handle and fast in computation. Possible modifications are discussed in the next section.

III. Modified Generation of Random Moves

For surface sampling we generated a random point ($\boldsymbol{\delta}$) on the surface of the $(D+1)$-dimensional sphere Δ (radius δ). As a generalization, we introduce *q-volume sampling*,

$$D = 2, 3: \qquad \boldsymbol{\delta}(q) \equiv t^q \boldsymbol{\delta}, \quad (8)$$

t being a random number uniform on $[0, 1]$ and $q > 0$ a given power. Then $q = 0$

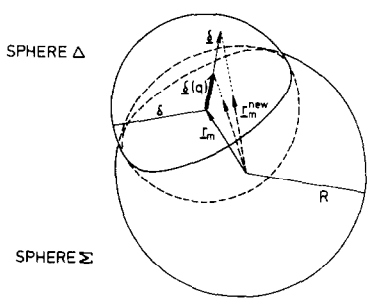

FIG. 1. Generation of random moves with spherical boundary conditions in 2 dimensions. For surface sampling, $\boldsymbol{\delta}$ (which points to the surface of Δ) is added to the current position $\mathbf{r}_m$ and the result projected back to Σ. For q-volume sampling, $\boldsymbol{\delta}$ is shortened to $\boldsymbol{\delta}(q) = \boldsymbol{\delta}t^q$, added to $\mathbf{r}_m$ and projected back to Σ.

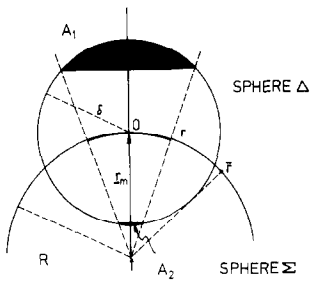

FIG. 2. To calculate the probability distribution of displacements for 2-dimensional surface sampling, the old position $\mathbf{r}_m$ is put into the north pole. The probability $P_{0,2}(r, \delta, R)$ to generate a displacement within distance r from $\mathbf{r}_m$ is given by the ratio of shaded surface $(A_1 + A_2)$ to total surface of Δ. The dashed line tangential to Δ corresponds to the maximum displacement $\bar{r}$, for which $A_1 + A_2$ covers the whole surface of Δ, and accordingly $P_{0,2}(\bar{r}, \delta, R) = 1$.

formally corresponds to surface sampling, $q > 0$ yields random points within the volume of sphere Δ, the weighting of the distances up to δ depending on q. Equation (7) remains valid if δ is replaced by $\delta(q)$.

For $D = 2$, we start with the results for surface sampling. The probability to generate a displacement smaller than r (measured on $\sum$) is given by

$$\begin{aligned} P_{0,2}(r, \delta, R) &= [A_1(r/R) + A_2(r/R)]/4\pi\delta^2, \qquad \text{if} \quad r < \bar{r}, \\ &= 1, \qquad\qquad\qquad\qquad\quad \text{if} \quad r \geqslant \bar{r}; \qquad \bar{r} = R \sin^{-1}(\delta/R). \end{aligned} \tag{9}$$

See Fig. 2. The first index of $P_{0,2}$ refers to q, the second to D. Analytical calculation yields

$$P_{0,2}(r, \delta, R) = 1 - \cos(r/R)(1 - [(R/\delta)\sin(r/R)]^2)^{1/2}, \qquad r < \bar{r}. \tag{10a}$$

For SBC, usually $\delta \ll R$. Thus, taking the limit $(\delta/R) \to 0$ results in an excellent approximation of $P_{0,2}$:

$$P^{\lim}_{0,2}(r, \delta) \equiv \lim_{(\delta/R)\to 0} P_{0,2}(r, \delta, R) = 1 - [1 - (r/\delta)^2]^{1/2}, \qquad r < \bar{r}_{\lim} = \delta. \tag{10b}$$

Differentiating (10a) with respect to r yields the probability density

$$\begin{aligned} p_{0,2}(r, \delta, R) &\equiv \partial P_{0,2}(r, \delta, R)/\partial r \\ &= (1/R)\sin(r/R)[1 + (R/\delta)^2 \cos(2r/R)] \\ &\qquad \times (1 - (R/\delta)\sin(r/R)]^2)^{-1/2}, \qquad r < \bar{r} \\ &= 0, \qquad\qquad\qquad\qquad\qquad\qquad r \geqslant \bar{r}. \end{aligned} \tag{11a}$$

See Fig. 3a. In the limit $(\delta/R) \to 0$,

$$p^{\lim}_{0,2}(r, \delta) = (r/\delta^2)[1 - (r/\delta)^2]^{-1/2}, \qquad r < \delta. \tag{11b}$$

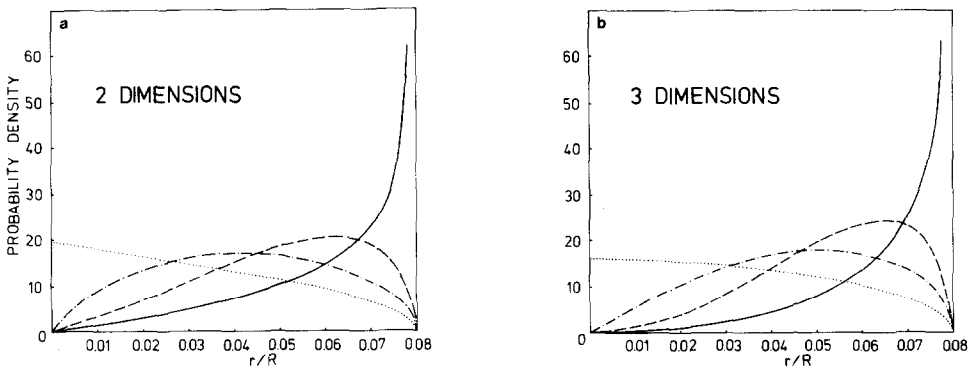

FIG. 3. Probability distributions $p_{q,D}(r, \delta, R)$ of displacements generated with q-volume sampling for SBC. (a) $D = 2$; (b) $D = 3$; (—) $q = 0$, (– –) $q = \frac{1}{4}$, (– · –) $q = \frac{1}{2}$, (⋯) $q = 1$. In fact, $q = 0$ (—) means surface sampling, but is considered as a special case of q-volume sampling for consistency reasons. All curves have been obtained by Monte Carlo runs, the spread being within drawing accuracy. The *shape* of the curves is almost independent of the actual choice of δ/R, provided $\delta/R \ll 1$(δ/R being 0.08 in Fig. 3).

Accordingly, surface sampling favours large displacements. When r approaches $\bar{r}$, $p_{0,2}$ diverges as $(\bar{r} - r)^{-1/2}$. All types of *q-volume sampling* provide some remedy for this fact by putting more weight on small displacements. For explicit calculations, we consider the points within the volume of sphere Δ. Their distance from the center of Δ is denoted b, $0 \leqslant b \leqslant \delta$. Using a random variable t uniform on $[0, 1]$, (8) yields for the density of random points $b = \delta t^q$ on $[0, \delta]$

$$\rho_b(q) = [b^{(1-q)/q}\, \delta^{-1/q}]/q. \tag{12}$$

Uniform sampling within the volume of the $(D + 1)$-dimensional sphere Δ means that ρ_b has to be proportional to b^D. Accordingly, the relation

$$q = 1/(D + 1) \tag{13}$$

must be fullfilled for *uniform volume sampling*. By inspection of Fig. 2, one can see that $P_{q,D}$ can be calculated from $P_{0,D}$ for any q:

$$P_{q,D}(r, \delta, R) = \int_0^\delta P_{0,D}(r, b, R)\, \rho_b(q)\, db. \tag{14}$$

Using $P_{0,2}$, Eq. (10a), one gets, e.g.,

$$P_{1/3,2}(r, \delta, R) = 1 - \cos(r/R)(1 - [(R/\delta)\sin(r/R)]^2)^{3/2}, \qquad r < \bar{r}, \tag{15a}$$

for uniform volume sampling in two dimensions. In the limit,

$$P^{\lim}_{1/3,2}(r, \delta) = 1 - [1 - (r/\delta)^2]^{3/2}, \qquad r < \delta. \tag{15b}$$

Differentiation yields for the respective probability densities

$$p_{1/3,2}(r, \delta, R) = (1/R)\sin(r/R)\{1 + (R/\delta)^2[3 - 4\sin^2(r/R)]\} \times \{1 - [(R/\delta)\sin(r/R)]^2\}^{1/2}, \qquad r < \bar{r}; \tag{16a}$$

$$p^{\lim}_{1/3,2}(r, \delta) = 3(r/\delta^2)[1 - (r/\delta)^2]^{1/2}, \qquad r < \delta. \tag{16b}$$

The quantities $P^{\lim}_{q,3}$ and $p^{\lim}_{q,3}$ can also be calculated. For instance,

$$p^{\lim}_{0,3}(r, \delta) = (4r/\pi\delta)\, p^{\lim}_{0,2}(r, \delta). \tag{17}$$

Figs. 3a and b display the Monte Carlo results for $p_{q,2}$ and $p_{q,3}$, respectively. In both figures, (δ/R) is 0.08, the cases $q = 0$, $\frac{1}{4}$, $\frac{1}{2}$, and 1 being included. The curves agree with the theoretical $p^{\lim}_{q,D}$ within Monte Carlo accuracy. Table I shows the efficiency of the selected algorithms for surface sampling and q-volume sampling for several q. Incidentally, the results $P^{\lim}_{q,D}$ and $p^{\lim}_{q,D}$ are exact if the described sampling procedure is used for displacements in Euclidean space and not on the surface of Σ. Thus, surface sampling and q-volume sampling can also be used for periodic boundary conditions.

Figs. 3a and b show that only surface sampling favours large distances. In the other cases exhibited, p is zero and thus continuous at $r = \bar{r}$. Now, we consider the displacement probability $\bar{p}_{q,D}$ per unit space on the surface of Σ. Instead of r, we differentiate with respect to V. Thus,

$$\bar{p}_{q,D}(r, \delta, R) = \partial P_{q,D}(r, \delta, R)/\partial V = p_{q,D}[\partial V/\partial r]^{-1};$$
$$D = 2: \quad \partial V/\partial r = 2\pi R \sin(r/R), \qquad D = 3: \quad \partial V/\partial r = 4\pi R^2 \sin^2(r/R). \tag{18}$$

TABLE I

Average Number of Variates and Roots per Trial when Generating a Random Displacement for SBC

q	D	Variates	Square roots	Cubic roots
0	2	2.55	3.27	0
$\frac{1}{4}$	2	3.55	5.27	0
$\frac{1}{3}$	2	3.55	3.27	1
$\frac{1}{3}$, CR[a]	2	5.73	2.91	0
$\frac{1}{2}$	2	3.55	4.27	0
1	2	3.55	3.27	0
2	2	3.55	3.27	0
0	3	5.09	4.55	0
$\frac{1}{4}$	3	6.09	6.55	0
$\frac{1}{4}$, CR[a]	3	12.97	5.33	0
$\frac{1}{2}$	3	6.09	5.55	0
1	3	6.09	4.55	0
2	3	6.09	4.55	0

[a] Uniform volume sampling can also be accomplished by a crude method CR, i.e., sampling uniformly in a cube and cutting out the inscribed sphere Δ.

TABLE II

Values of the Displacement Probability per Unit Space on Σ

		(r/δ)				
q	D	0	0.25	0.50	0.75	1.0
0	2	1.0	1.03	1.15	1.51	∞
$\frac{1}{4}$	2	2.0	2.19	2.39	2.22	0
$\frac{1}{3}$	2	3.0	2.90	2.60	1.98	0
$\frac{1}{2}$	2	∞	4.13	2.63	1.59	0
1	2	∞	5.27	2.09	0.96	0
0	3	1.0	1.03	1.15	1.51	∞
$\frac{1}{4}$	3	4.0	3.87	3.46	2.65	0
$\frac{1}{2}$	3	∞	10.54	4.19	1.93	0
1	3	∞	15.49	3.46	1.18	0

Note. Probability density $\bar{p}^{\lim}_{q,S}(r, \delta)\, k_D$ for surface sampling ($q = 0$) and q-volume sampling where $k_2 = 2\pi\delta^2$ and $k_3 = \pi^2\delta^3$ are chosen to make $\bar{p}^{\lim}_{0,D}$ equal to one for $(r/\delta) = 0$.

For instance, $p_{0,2}$ of Eq. (11a) transforms to

$$\bar{p}_{0,2}(r, \delta, R) = (2\pi R^2)^{-1}[1 + (R/\delta)^2 \cos(2r/R)](1 - [(R/\delta)\sin(r/R)]^2)^{-1/2}, \qquad r < \bar{r}. \tag{19}$$

The divergence at $r = \bar{r}$ remains. For $r \ll \bar{r}$, however, $\bar{p}_{0,2}$ is approximately constant, thus reflecting the uniform distribution (on $\sum$) for small displacement. Table II shows values of $\bar{p}^{\lim}_{q,D}$ for various q, Eq. (18) being inserted in the results for $p^{\lim}_{q,D}$ obtained analytically. For instance, one can see that the choice $q = 1/4$ yields an almost uniform random move up to $\bar{r}$, especially in two dimensions. On the other hand, surface sampling is the simplest and fastest procedure considered, cf. Table I. Actual Monte Carlo runs are necessary for a final decision as to which method to adopt for a given potential.

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