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New Boundary Conditions for Computer Experiments of Thermodynamic Systems

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In this paper, a new kind of boundary conditions for computer experiments of thermodynamic systems is introduced. The merits of using a D-dimensional system as the surface of a $(D+1)$-dimensional sphere are discussed in general. Finally it is shown that these "spherical boundary conditions" have some advantages compared with others.

1. INTRODUCTION

In computer experiments, the number N of molecules which can be handled is typically 100–1000. Comparison with theory or real experiments is delicate: Usually, theory yields the thermodynamic limit and experiments deal with macroscopic numbers of particles. There are two possible ways to estimate the thermodynamic limit from the results of computer experiments:

(a) using different N in various computer experiments and trying to extrapolate to $N \to \infty$ [1–3],

(b) using theoretical knowledge of the deviation from the thermodynamic limit [4–6].

Despite of all the progress made since the introduction of molecular dynamics (MD) and Monte Carlo (MC) the microscopic nature of computer experiments remains a problem [7]. In the present paper, this problem is attacked by introducing a new kind of boundary conditions (BC) for computer experiments, the spherical BC. First, the known BC and their geometric properties will be considered (Section 2). In Section 3, the new BC are defined. Then the finite-size effects are investigated for the known BC (Section 4) and the new BC (Section 5). Section 6 deals with the realization of computer experiments with spherical BC. As a typical quantity, the pressure P of classical one-component equilibrium systems will be studied. The molecules are assumed to interact via central two-body forces which are spherically symmetrical. The canonical ensemble (for MC) and the microcanonical ensemble (for MD) will be considered throughout this paper.

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2. FIXED AND PERIODIC BOUNDARY CONDITIONS

The finite number N of particles induces some kind of boundary which is absent in the thermodynamic limit. It seems to be natural to enclose the volume in a vessel (fixed BC). For $N \approx 100$, however, a great portion of the molecules is close to the surface, and one can expect that the bulk properties are not well reproduced (see also Section 4). Thus, another kind of BC has been used in the literature [8]: The periodic BC (toroidal BC). Besides the basic volume, the space is now filled by periodic images of this basic cell. Thus the system is formally infinite, and there is no surface. Yet, each of the N original particles has an infinite number of "ghost particles" and the distance between two particles is not defined uniquely. To overcome this difficulty, either a cutoff radius of the interaction potential can be used, or the minimum of the possible distances between two particles is defined as the "real distance" (minimum image convention). Both procedures have the disadvantage that the force between two particles becomes a discontinuous function of their location.

Another possibility to imagine the periodical BC is to embed the D-dimensional system in a space of $D+1$ dimensions, the element of volume remaining Euclidean. For instance, a one-dimensional box becomes an annulus, a two-dimensional box becomes a torus (hence the name "toroidal BC"). From this point of view, there are no ghost particles, but the distance between two molecules is also not uniquely defined since there is an infinite number of geodesic curves between two particles ($D > 1$).

Table I shows the important geometric properties of the infinite Euclidean space and of a finite volume with fixed and periodic BC. For the last column (spherical BC), see Section 3. "Homogeneous" and "isotropic" mean that there is no differentiation concerning the importance of certain points and directions, respectively. The property "singly connected" will become important in Section 4. It means that every closed curve can be contracted continuously to a single point. This is not the case for periodic BC; consider, e.g., a circle which winds around a torus [4].

TABLE I

Geometrical Properties of a D-Dimensional Cell ($D > 1$)[a] for Various Boundary Conditions

Property	Infinite volume	Fixed BC	Periodic BC	Spherical BC
Surface absent	+	−	+	+
Homogeneous	+	−	+	+
Isotropic	+	−	−	+
Euclidean	+	+	+	−
Singly connected	+	+	−	+
No. of particles	∞	N	$\infty (N)$[b]	N
No. of distances between two points	1	1	∞	2

[a] For $D = 1$, there are several exceptions.

[b] Two equivalent points of view of the same BC; see Section 2.

3. SPHERICAL BOUNDARY CONDITIONS

Table I shows that the geometric properties of the thermodynamic limit are only partly reproduced by the fixed and periodic BC, respectively. The interpretation of a D-dimensional system with periodic BC as a generalized torus embedded in a $(D+1)$-dimensional space suggests the definition of a new kind of BC, the "spherical BC": The D-dimensional cell forms the surface of a $(D+1)$-dimensional sphere (with the usual spherical trigonometry).

Inspection of Table I shows that the properties of the spherical BC yield the best overall agreement with the infinite cell. This is due to the high symmetry of the surface of a sphere. Two distinct points of the sphere have only two distances corresponding to the two segments of the great circle. Thus, besides using a cutoff radius and the minimum image convention, a further possibility (which may be called "double distance convention") exists for spherical BC: If the distances between two particles are called r_{min} and r_{max} and, e.g., a Lennard-Jones potential (parameters ε, σ) is assumed, it is convenient to define the "double distance" potential U as

$$U = 4\varepsilon\left[\left(\frac{\sigma}{r_{\text{min}}}\right)^{12} + \left(\frac{\sigma}{r_{\text{max}}}\right)^{12} - \left(\frac{\sigma}{r_{\text{min}}}\right)^{6} - \left(\frac{\sigma}{r_{\text{max}}}\right)^{6}\right]. \tag{1}$$

If R is the radius of the $(D+1)$-dimensional sphere defining the spherical BC, $r_{\text{max}} = 2\pi R - r_{\text{min}}$. U has the property that two molecules which are very close to one another interact with the usual Lennard–Jones potential since the terms with r_{min} are predominant. For increasing distance, the force decreases faster than usual. The two particles correspond to antipodal points if $r_{\text{min}} = r_{\text{max}} = \pi R$. The continuous force vanishes in this case ($U \neq 0$). Thus, antipodal points simulate the case in the thermodynamic limit where two particles have infinite distance. In the thermodynamic limit ($R \to \infty$), r_{max} becomes infinite in any case, and only one meaningful distance (r_{min}) is left. If the terms with r_{max} are also absent for finite R, this corresponds to the minimum image convention, the force being discontinuous at $r_{\text{min}} = \pi R$. Further reduction to $U = 0$ if $r_{\text{min}} > r_{\text{co}}$ results in a cutoff radius, the potential being discontinuous at $r_{\text{min}} = r_{\text{co}}$. Thus, the minimum image convention is a special case of using a cutoff radius ($r_{\text{co}} = \pi R$) for spherical BC.

We have discussed some properties of the spherical BC. The essential difference, however, to all other BC lies in the fact that the system is not Euclidean for spherical BC. This will be investigated in Section 5.

4. FINITE-SIZE EFFECTS OF THE PRESSURE

First we consider the virial expansion of the pressure P in the thermodynamic limit:

$$\left(\frac{P}{\rho kT}\right) = 1 + \sum_{i=2}^{\infty} B_i \rho^{i-1}. \tag{2}$$

ρ is the limit of the number density N/V, k is Boltzmann's constant, and T is the absolute temperature. The virial coefficients B_i are constants and consists of Mayer cluster integrals, e.g.,

$$\begin{aligned} B_2 &= \lim_{V\to\infty} B_2^+(\tilde{V}), \qquad B_3 = \lim_{V\to\infty} B_3^+(\tilde{V}), \\ B_2^+(\tilde{V}) &\doteqdot -\frac{1}{2V}\int_V\int_V d\mathbf{r}_1\, d\mathbf{r}_2 f_{12}, \\ B_3^+(\tilde{V}) &\doteqdot -\frac{1}{3V}\int_V\int_V\int_V d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 f_{12} f_{13} f_{23}, \\ f_{ij} &\doteqdot \exp[-U(r_{ij})/kT] - 1. \end{aligned} \tag{3}$$

$U(r_{ij})$ is the spherically symmetric pair potential. Equation (3) also defines volume-dependent cluster integrals if the thermodynamic limit is not taken. The symbol $\tilde{V}$ indicates that the integrals are functions not only of the value V, but also of the shape of the volume including the BC (for spherical BC, this shape is of course always the same). This implicit volume dependence is a very important feature of finite-size effects [4] and will be considered later. Now the simpler explicit number dependence will be studied. The pressure due to this N dependence can be written as [4–6]

$$\left(\frac{P}{\rho kT}\right) = 1 + \sum_{i=2}^{\infty} B_i(N)\rho^{i-1}. \tag{4}$$

The $B_i(N)$ depend on the ensemble, but not on the shape of the volume. For the canonical NVT ensemble,

$$\begin{aligned} B_2(N) &= \left(1-\frac{1}{N}\right) B_2, \\ B_3(N) &= \left(1-\frac{1}{N}\right)\left(1-\frac{2}{N}\right) B_3 + \frac{2}{N}\left(1-\frac{1}{N}\right) B_2^2, \\ B_i(N) &= B_i + (a_i/N) + O(1/N^2), \qquad i \geqslant 2. \end{aligned} \tag{5}$$

The a_i are constants. Thus, a MC-experiment (NVT) yields the explicit number dependence

$$\left(\frac{P}{\rho kT}-1\right)_{\mathrm{MC}} = \left(\frac{P}{\rho kT}-1\right)_{\mathrm{limit}} \times \left[1 + \frac{a(\rho)}{N} + O\left(\frac{1}{N^2}\right)\right]. \tag{6}$$

If we restrict ourselves for the moment to hard disks and hard spheres, the microcanonical and canonical ensembles are identical. Thus the MD and MC values are directly comparable using the relation [1]

$$\left(\frac{P}{\rho kT}-1\right)_{\mathrm{MD}} = \frac{N}{N-1}\left(\frac{P}{\rho kT}-1\right)_{\mathrm{MC}}, \tag{7}$$

TABLE II

$|B_i(N) - B_i|/B_i$ for Hard Disks and Spheres (NVT Ensemble)

	N(disks)		N(spheres)	
i	100	200	100	200
2	−0.01000	−0.00500	−0.01000	−0.00500
3	−0.00448	−0.00223	+0.00188	+0.00097
4	−0.00278	−0.00142	−0.00258	−0.00149
5	−0.00265	−0.00129	−0.00273	−0.00060

the factor $N/(N-1)$ being due to the fact that the center of mass is fixed additionally in MD for periodic and spherical BC. Thus also for MD Eq. (6) is valid with $|a(\rho)+1|$ instead of $a(\rho)$. Since the $B_i(N)$ are functions of $(B_2, \ldots, B_i)$, the simple N dependence can in principle be calculated from the thermodynamic limit itself. Since for hard disks and spheres the B_i up to B_5 are known very accurately [9–11], $B_i(N)$ up to $B_5(N)$ can be given accurately (Table II). Table II shows that the explicit N dependence is especially systematic for disks and the corrections to the thermodynamic limit are small (less than 1% for $N > 100$).

Now we also consider the volume dependence due to the cluster integrals themselves; compare Eq. (3). Using the definition

$$B_i(\tilde{V}) = B_i^+(\tilde{V}) - \frac{V}{i-1}\frac{d}{dV}B_i^+(\tilde{V}), \tag{8}$$

where the shape of V remains constant during the differentiation, the second and third virial coefficients including all finite-size effects become in the NVT ensemble

$$\begin{aligned} B_2(N, \tilde{V}) &= \left(1 - \frac{1}{N}\right) B_2(\tilde{V}), \\ B_3(N, \tilde{V}) &= \left(1 - \frac{1}{N}\right)\left(1 - \frac{2}{N}\right) B_3(\tilde{V}) + \frac{2}{V}\left(1 - \frac{1}{N}\right) B_2^+(\tilde{V})\, B_2(\tilde{V}). \end{aligned} \tag{9}$$

This can be derived from the results of [4]. Not much can be said about the convergence of the virial expansion of the pressure. Even in the case of the thermodynamic limit, Eq. (2), our knowledge is very restricted [12]. It can be hoped that the virial expansions make sense for the entire fluid range up to the (first) phase transition.

Contrary to the low-order $B_i(N)$, the $B_i(\tilde{V})$ are very complicated to calculate even for very simple systems. For rigid BC, the deviation of $B_i(\tilde{V})$ from the thermodynamic limit comes from the existence of a surface (compare Table I) which induces the properties "inhomogeneous" and "anisotropic." Due to the surface effects, the main volume dependence is proportional to the ratio (surface/volume), i.e., $V^{-1/D}$ for a D-dimensional system. Thus,

$$[B_i(\tilde{V}) - B_i]/B_i \approx c_i V^{-1/D}, \qquad \text{fixed BC.} \tag{10}$$

For a given ρ, $V^{-1/D}$ corresponds to $N^{-1/D}$. On the other hand, N^{-1} is the leading term for the deviation of $B_i(N)$ from B_i, see Eq. (5). Thus, especially for $D > 2$ the implicit dependence is predominating for fixed BC. This leads to a considerable deviation from the thermodynamic limit as expected.

For periodic BC, a surface is absent. The implicit volume dependence comes from the fact that the volume is not singly connected (see Table I). The line segment between two identical particles (particle, ghost particle) can be interpreted as a closed curve through the particle. This curve cannot be contracted further. The minimum distance with this property is the minimum side length $l_{\min}$ of the rectangular periodic cell. Lebowitz and Percus [4] showed that

$$B_i(\tilde{V}) = B_i \qquad \text{for} \quad i \leqslant l_{\min}/a, \quad \text{periodic BC,} \tag{11}$$

a being the range of the intermolecular forces. The value of $[B_i(\tilde{V}) - B_i]$ for greater i cannot be calculated. For hard spheres, Eq. (11) means that about the first five virial coefficients $B_i(\tilde{V})$ remain unchanged for $N \approx 100$ and high fluid densities. This is a considerable advantage over the fixed BC. For long-range potentials, the gain is not so obvious. Furthermore, at high densities many virial coefficients contribute to the equation of state, and the finite-size effects cannot be evaluated then. Experience shows that the periodic BC are very good for one-phase systems but yield inaccurate results close to phase transitions [12, 13]. This agrees with the intuitive argument that the periodic cell favours solidlike structures, especially if N is chosen to fit into a crystal structure. For instance, this influences the configurations sampled close to the fluid–solid transition for hard disks or spheres.

5. Volume-Dependent Virial Coefficients for the Spherical Boundary Conditions

For the spherical BC, the property "non-Euclidean" alone is responsible for the volume dependence of $B_i^+(\tilde{V})$ and of $B_i(\tilde{V})$. The cluster integrals (Eqs. (3), (8)) have to be evaluated for non-Euclidean coordinates (see the Appendix for explicit calculations). Trigonometric functions such as $\sin\theta = \theta - \theta^3/6 + O(\theta^5)$ come in. Since every second power of θ is missing in the power series, the virial coefficients become

$$[B_i(\tilde{V}) - B_i]/B_i = \bar{c}_i V^{-2/D} + O(V^{-4/D}), \qquad D > 1, \tag{12}$$

instead of the dependence $(c_i V^{-1/D})$ for fixed BC (see Eq. (10)). The volume dependence starts with $i = 2$ and is a systematic function of V as in the case of fixed BC.

TABLE III

Finite-Size Effects of the Pressure for Spherical BC

Dim. D	Explicit	Implicit	Combined effects
2	$N^{-1}, N^{-2}, \ldots$	$N^{-1}, N^{-2}, \ldots$	$N^{-1}, N^{-2}, \ldots$
3	$N^{-1}, N^{-2}, \ldots$	$N^{-2/3}, N^{-4/3}, \ldots$	$N^{-2/3}, N^{-1}, N^{-4/3}, \ldots$

The advantage of the spherical BC is the factor $V^{-2/D}$ (or $N^{-2/D}$ for given ρ) instead of $N^{-1/D}$, which means a much smaller implicit volume dependence.

Table III shows the powers of N which can be expected due to finite-size effects (spherical BC); compare Eqs. (5), (9), and (12). It is realistic to assume that for $N > 100$ all dependencies starting with $N^{-4/3}$ are within the statistical error of P obtained by computer experiments. This means that in three dimensions it is possible to fit the pressure data obtained with spherical BC for different N to a curve $P_{\text{limit}} + \alpha N^{-2/3} + \beta N^{-1}$. The term βN^{-1} only comes from the explicit N dependence. Therefore, βN^{-1} can be estimated for hard spheres (see Table II), which simplifies the problem further.

In two dimensions, the situation is even simpler. Both explicit and implicit dependencies yield the same powers of N. Thus, a linear fit in $1/N$ is sufficient to estimate the thermodynamic limit:

$$\left(\frac{P}{\rho kT}\right)_{\text{spher. BC}} = \left(\frac{P}{\rho kT}\right)_{\text{limit}} + \frac{f(\rho)}{N} + O\left(\frac{1}{N^2}\right). \tag{13}$$

This section has shown that spherical BC may be more convenient for computer experiments than the known BC. In a certain sense, the spherical BC and the periodical BC are complementary: The periodic BC favour solid configurations, the spherical BC favour fluid configurations. No perfect crystal structure can be generated for spherical BC except for singular cases (e.g., 12 disks forming a dodecahedron on the surface of a sphere). Therefore it might be attractive to compare the results obtained by periodic BC and spherical BC, respectively.

6. THE ACCOMPLISHMENT OF COMPUTER EXPERIMENTS USING SPHERICAL BOUNDARY CONDITIONS (*NVT* ENSEMBLE)

Calculation of the pressure from computer experiments with spherical BC has been left open up to now. We consider, e.g., the relation

$$\left(\frac{P}{\rho kT}\right) = 1 + \rho B_2\, g(\sigma), \tag{14}$$

which is valid for D-dimensional hard spheres (with diameter σ) in the thermodynamic limit [9]. Is it also valid for spherical BC? If one checks the derivation of Eq. (14) (see, e.g., [14]), one can see that the pressure equation of a spherically symmetric potential $U(r)$ becomes

$$\left(\frac{P}{\rho kT}\right)=1-\frac{\rho}{2DkT}\int_V r\frac{dU(r)}{dr}g(r)\,d^Dr \tag{15}$$

for spherical BC. This is formally the same as that for the thermodynamic limit. However, the volume element d^Dr is not Euclidean now; compare the Appendix. The radial distribution function $g(r)$ is defined as usual, but also with the non-Euclidean volume element. For the D-dimensional hard-sphere potential, Eq. (15) further reduces to

$$\left(\frac{P}{\rho kT}\right)=1+\left[\frac{\sin(\sigma/R)}{(\sigma/R)}\right]^{D-1}\rho B_2\,g(\sigma). \tag{16}$$

Equation (16) is the counterpart of Eq. (14), R being the radius of the $(D+1)$-dimensional sphere; see Section 3. $g(\sigma)$ can be evaluated in computer experiments as usual. By means of (16), it is possible to obtain the hard-sphere pressure in computer experiments for spherical BC.

It is interesting to expand the canonical $g(r)$ in powers of ρ,

$$g(r_{12})=\left[1-\frac{1}{N}\right]\left\{1+\rho\left[\frac{2B_2^+(\tilde{V})}{N}+\left(1-\frac{2}{N}\right)b_{12}(r_{12})\right]+O(\rho^2)\right\}, \tag{17}$$

where the notation $b_{12}(r_{12})$ is due to [9]. For D-dimensional hard spheres (diameter σ), $b_{12}(r_{12})$ is the volume of intersection of two spheres (radius σ) at distance r_{12}. Equation (16) together with Eq. (17) yields an expansion of $(P/\rho kT)$ in powers of ρ which must yield the $B_i(N,\tilde{V})$; see (9). Indeed, (16) and (17) result in

$$\begin{aligned}B_2(N,\tilde{V})&=\left(1-\frac{1}{N}\right)B_2\left[\frac{\sin(\sigma/R)}{(\sigma/R)}\right]^{D-1},\\ B_3(N,\tilde{V})&=\left(1-\frac{1}{N}\right)\left(1-\frac{2}{N}\right)b_{12}(\sigma)B_2\left[\frac{\sin(\sigma/R)}{(\sigma/R)}\right]^{D-1}\\ &\quad+\frac{2}{N}\left(1-\frac{1}{N}\right)B_2^+(\tilde{V})B_2\left[\frac{\sin(\sigma/R)}{(\sigma/R)}\right]^{D-1}.\end{aligned} \tag{18}$$

This corresponds to Eq. (9) with

$$B_2(\tilde{V})=B_2\left[\frac{\sin(\sigma/R)}{(\sigma/R)}\right]^{D-1}, \tag{19}$$

$$B_3(\tilde{V})=b_{12}(\sigma)B_2(\tilde{V}). \tag{20}$$

Equation (19) has been checked explicitly for $D = 2, 3$ (see the Appendix). It can also be used to simplify (16). Equation (20) is the generalization of

$$b_{12}(\sigma)\, B_2 = B_3. \tag{21}$$

Equation (21) is valid in the thermodynamic limit [9, 10]. Thus, the equivalence between the expansion of $(P/\rho kT)$ in Mayer graphs (Eq. (3)) and Mayer–Montroll graphs as, e.g., $b_{12}(\sigma)$ (compare Eqs. (14) and (17)) yields generalized relations between the cluster integrals for spherical BC.

To test the spherical BC for the first time, a MC computer experiment will be done for hard disks at high fluid densities and the fluid–solid transition. For hard disks, $B_2^+(\tilde{V})$ and $B_2(\tilde{V})$ are known analytically; see Eq. (19) and the Appendix. By means of Eq. (20) and $b_{12}(r)$ calculated for disks in the Appendix, $B_3(\tilde{V})$ is also known analytically for hard disks. Expansion in powers of $(4\pi R^2)^{-1} = V^{-1}$ yields

$$\begin{aligned} B_2(\tilde{V})/B_2 &= 1 - \tfrac{4}{3} B_2 V^{-1} + O(V^{-2}), \\ B_3(\tilde{V})/B_3 &= 1 - 1.295 B_2 V^{-1} + O(V^{-2}). \end{aligned} \tag{22}$$

Thus $B_2(N, \tilde{V})$ and $B_3(N, \tilde{V})$ are also known (see Eq. (9)):

$$\begin{aligned} B_2(N, \tilde{V})/B_2 &= 1 - (1 + \tfrac{4}{3} B_2 \rho)\, N^{-1} + O(N^{-2}), \\ B_3(N, \tilde{V})/B_3 &= 1 - (0.442 + 1.295 B_2 \rho)\, N^{-1} + O(N^{-2}). \end{aligned} \tag{24}$$

For $N = 100$ and a typical high fluid density (1/1.40 of the close-packed density) this yields

$$B_2(N, \tilde{V})/B_2 = 0.973, \qquad B_3(N, \tilde{V})/B_3 = 0.979. \tag{24}$$

Therefore, the deviation of the pressure from the thermodynamic limit seems to be 2–3% in this case. For $N > 300$, the pressure is expected to lie within the statistical error of P (which is about 1%) for the hard-disk fluid even close to the fluid–solid transition. Thus, the spherical BC are not only interesting from a general point of view (Section 3), but are also very promising for a special system which can be treated mathematically.

APPENDIX

The spherical BC imply calculations using non-Euclidean geometry. Some examples are given in this appendix. Most calculations are carried out for dimension $D = 2$. The case $D = 3$ is more complicated but is not different from a qualitative point of view.

For $D = 2$, the finite cell is the surface of a three-dimensional sphere of radius R.

The angles are denoted θ (colatitude) and φ (longitude) as usual. The two-dimensional element of volume is

$$dr^2 = R^2 \sin\theta \, d\theta \, d\varphi = [R \sin(r/R)] \, dr \, d\varphi, \tag{A1}$$

where $r = \theta R \leqslant \pi R$ is the (geodesic) distance of a point from the north pole of the sphere. The distance between two points i, j is given by

$$\cos\left(\frac{r_{ij}}{R}\right) = \cos\left(\frac{r_i}{R}\right) \cos\left(\frac{r_j}{R}\right) + \sin\left(\frac{r_i}{R}\right) \sin\left(\frac{r_j}{R}\right) \cos(\varphi_{ij}), \tag{A2}$$

φ_{ij} being $(\varphi_j - \varphi_i)$. Expanding the trigonometric functions results in the following r_{ij} ($r_{\min}$ or $r_{\max}$; compare (1)):

$$\begin{aligned} r_{ij} &= r_{ij}^{\mathrm{Eucl}} \left\{ 1 - \frac{1}{6R^2} \left[\frac{r_i r_j \sin\varphi_{ij}}{r_{ij}^{\mathrm{Eucl}}} \right]^2 + O\left(\frac{1}{R^4}\right) \right\}, \\ (r_{ij}^{\mathrm{Eucl}})^2 &= r_i^2 + r_j^2 - 2 r_i r_j \cos\varphi_{ij}. \end{aligned} \tag{A3}$$

Now the coefficients $B_2^+(\tilde{V})$, $B_2(\tilde{V})$, $B_3^+(\tilde{V})$, and $B_3(\tilde{V})$ will be investigated for hard disks (geodesic diameter σ); compare Eqs. (3), (8). The potential is characterized by

$$\begin{aligned} f_{12}(r_{12}) &= -1, & r_{12} &< \sigma, \\ &= 0, & r_{12} &\geqslant \sigma. \end{aligned} \tag{A4}$$

Using Eq. (3) it follows that

$$B_2^+(\tilde{V}) = \pi \int_0^\sigma dr \, [R \sin(r/R)] = B_2 \left[\frac{\sin(\sigma/2R)}{(\sigma/2R)} \right]^2, \tag{A5}$$

if $R\pi > \sigma$, B_2 being $\frac{1}{2}\pi\sigma^2$. From Eq. (8) it follows that

$$B_2(\tilde{V}) = B_2 \left[\frac{\sin(\sigma/R)}{(\sigma/R)} \right]. \tag{A6}$$

Incidentally, the determination of $B_2^+(\tilde{V})$ and $B_2(\tilde{V})$ for hard spheres is also very simple, the result being

$$B_2^+(\tilde{V}) = 6B_2 \left[\frac{(2\sigma/R) - \sin(2\sigma/R)}{(2\sigma/R)^2} \right], \qquad B_2(\tilde{V}) = B_2 \left[\frac{\sin(\sigma/R)}{(\sigma/R)} \right]^2 \tag{A7}$$

with $B_2 = \frac{2}{3}\pi\sigma^3$. Equations (A6) and (A7) check the general relation (19) for $D = 2$ and $D = 3$, respectively.

Now we concentrate again on hard disks. If $b_{12}(r)$ is the non-Euclidean area of intersection of two disks 1, 2 with geodesic radius σ and distance r ($r = r_{\min}$), $B_3^+(\tilde{V})$ can be simplified (see Eq. (3)):

$$B_3^+(\tilde{V}) = \frac{2\pi}{3} \int_0^{\sigma} dr\, b_{12}(r)[R \sin(r/R)]. \tag{A8}$$

The explicit calculation of $b_{12}(r)$, $0 \leqslant r \leqslant 2\sigma$, is very complicated. The result is

$$\begin{aligned} b_{12}(r) = 2R^2 \Big\{ &\pi(1 - \cos\beta) - 2 \sin^{-1} q \\ &+ |\cos\beta| \left[\sin^{-1}\left(\frac{q + \sin\beta}{1 + \sin\alpha}\right) + \sin^{-1}\left(\frac{q - \sin\beta}{1 - \sin\alpha}\right)\right]\Big\}, \end{aligned} \tag{A9}$$

$\alpha \doteqdot r/(2R)$, $\beta \doteqdot \sigma/R = (8B_2/V)^{1/2}$, $q \doteqdot \sin\alpha/\sin\beta$. If one expands $b_{12}(r)$ in powers of $1/R$ and introduces $z \doteqdot \alpha/\beta = r/(2\sigma)$, one gets, finally,

$$\begin{aligned} b_{12}(r) = 2\sigma^2 \Big\{ &[\cos^{-1} z - z(1 - z^2)^{1/2}] \\ &- \frac{\beta^2}{12} [\cos^{-1} z - z(1 - z^2)^{1/2} (3 - 2z^2)] + O(\beta^4)\Big\}, \end{aligned} \tag{A10}$$

$$b_{12}(\sigma) = B_2 \left[\left(\frac{4}{3} - \frac{3^{1/2}}{\pi}\right) + \frac{\beta^2}{6}\left(-\frac{2}{3} + \frac{5}{4}\frac{3^{1/2}}{\pi}\right) + O(\beta^4)\right].$$

The leading term is the Euclidean value; compare [15]. If one inserts (A10) in (A8), one obtains

$$B_3^+(\tilde{V}) = B_2^2 \left[\left(\frac{4}{3} - \frac{3^{1/2}}{\pi}\right) + \beta^2 \left(-\frac{2}{9} + \frac{3^{1/2}}{4\pi}\right) + O(\beta^4)\right]. \tag{A11}$$

Calculating $B_3(\tilde{V})$ via Eq. (8) yields an almost identical expression, except that the coefficient of β^2 is larger by a factor $\frac{3}{2}$. By means of (20) and using (A6) and (A9), it is even possible to obtain $B_3(\tilde{V})$ analytically for hard disks as claimed in Section 6.

Now we turn to the general case of spherically symmetric potentials of finite range a. From (3) it follows for $D = 2$ that

$$\begin{aligned} B_2^+(\tilde{V}) &= -\frac{1}{2V} \int_V \int_V d\mathbf{r}_1\, d\mathbf{r}_2 f_{12}(r_{12}) = -\frac{1}{2} \int_V d\mathbf{r}_2 f_{12}(r_{12}) \\ &= -\pi \int_0^{\min(a, \pi R)} dr_2\, [R \sin(r_2/R)] f_{12}(r_2). \end{aligned} \tag{A12}$$

In (A12), the double integral has been simplified to give a simple integral due to the "homogeneous" property of the spherical BC. Without loss of generality, the center of molecule 1 can be set on the north pole of the sphere. The last expression of (A12) comes from the "isotropic" property, which makes it possible to integrate over the angle φ_2. This is often done as an approximation for the other BC, but for the spherical BC this is exact. The upper limit of the last integral of (A12) is $\min(a, \pi R)$. If R is chosen to be greater than (a/π), this limit becomes independent of R. This will be assumed in the following. Then the only dependence on R comes from $[R \sin(r_2/R)]$. If one expands this term in powers of R^{-1}, one gets

$$B_2^+(\tilde{V}) = B_2 + c_2^+ R^{-2} + O(R^{-4}), \tag{A13}$$

where c_2^+ is an R-independent integral. Incidentally, Eq. (A13) does not depend on the condition $D = 2$. Since V is proportional to R^D, the expansion (A13) in powers of R^{-2} is generally an expansion in powers of $V^{-2/D}$; see Section 5. Now we turn to $B_3^+(\tilde{V})$ for $D = 2$.

$$B_3^+(\tilde{V}) = -\frac{2\pi}{3}\int_0^a dr_2\, [R \sin(r_2/R)] f_{12}(r_2) \int_V d\mathbf{r}_3 f_{13}(r_3) f_{23}(r_{23}). \tag{A14}$$

r_{ij} can be expanded in powers of R^{-2}; see (A3). Thus, $B_3^+(\tilde{V})$ is also a power series in R^{-2} eventually.

The above considerations can be generalized as follows: For a D-dimensional system of molecules with spherically symmetric potential of range a, the virial coefficients $B_i^+(\tilde{V})$ and $B_i(\tilde{V})$ can be expanded in a power series in $R^{-2} = V^{-2/D}$. The only condition is $R > \pi a$; i.e., the range of the potential does not cover the whole surface of the sphere. Even the case "spherically symmetric potential" is not a real restriction to the validity of the above results; this condition is only used in this paper for simplicity.

Last, the assumption of finite potential range is removed. If one takes a fixed cutoff radius a, the situation is the same as above, but then the results are biased even for $R \to \infty$. However, if one takes

$$r_{\text{cutoff}} = pR\pi, \qquad 0 < p \leqslant 1, \tag{A15}$$

the upper limits of the integrals (see, e.g., (A12)) are functions of R. This induces a further dependence on R. We study, e.g., the minimum image convention, $p = 1$. We choose a distance a beyond which only small long-range forces occur. This results in

$$r > a: \quad f_{12}(r) \cong U(r)/kT \cong cr^{-n}. \tag{A16}$$

If $D = 2$ and $R\pi > a$, it follows for a given T that

$$B_2^+(\tilde{V}) = -\pi \left\{ \int_0^a dr_2 [R \sin(r_2/R)] f_{12}(r_2) + c \int_a^{R\pi} dr_2 [R \sin(r_2/R)]\, r_2^{-n} \right\}. \tag{A17}$$

The last integral corresponds to a constant plus a value proportional to R^{2-n} (or R^{D-n} for general D and $n > D$). Thus one can also predict the finite-size behavior for spherical BC if the range of the potential is not finite. The general result for $B_i^+(\tilde{V})$ and $B_i(\tilde{V})$ is

$$B_i(\tilde{V}) = B_i + \alpha_i R^{-2} + \bar{\alpha}_i R^{D-n} + O(R^{-4}), \qquad n > D. \tag{A18}$$

Equation (A18) is valid not only for the minimum image convention, but also for any cutoff radius (A15) and the double distance convention, Eq. (1). Only the coefficients $\bar{\alpha}_i$ differ.

If $n = D + 2$ or $n \geqslant D + 4$, the term $\bar{\alpha}_i R^{D-n}$ can be included among $\alpha_i R^{-2}$ or $O(R^{-4})$, respectively. In these cases, the extrapolation $R \to \infty$ of results obtained by computer experiments can be done in the same way as for potentials with fixed finite range; see Eq. (A13) and Table III. If $n = D + 1$, the contribution from the long-range part of the potential (proportial to R^{-1}, i.e., $N^{-1/D}$ for a given density ρ) becomes the predominant finite-size effect. If $n = D + 3$, this term (proportional to $N^{-3/2}$) lies within the error of computer experiments for $D = 2$. For $D = 3$, the term is proportional to N^{-1} and thus can be ascribed formally to the explicit N dependence of $B_i(N, \tilde{V})$ for a given density ρ.

Experience shows that for periodical BC difficulties occur concerning finite-size effects of potentials with n too low. However, it is impossible to attack this problem mathematically. For spherical BC, this problem has been solved by means of Eq. (A18).

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