

Monte Carlo simulation for a gas of hard spheres in d -dimensional space: equilibrium structure and state equations

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We emphasize that using only a personal computer, it is possible to perform a Monte Carlo simulations in reasonable computing time find the equilibrium structure of a gas consisting of hard spheres in for a Euclidean multi-dimensional spaces. We study the equilibrium conditions and determine the equation of state for two to seven dimensions. The results show that the pressure is in agreement with different theoretical models based on the virial expansion As expected, when the dimension of the space increases, the system of hard spheres loses its structure and the pressure decreases.

Keywords: Monte Carlo simulations; phase equilibria; fluids; thermodynamics.

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1. Introduction

A standard and nontrivial model for studying the equilibrium properties of a liquid is the hard sphere (HS) system [1]. The hard sphere model serves as a reference for the study of more complex systems, for example multicomponent fluid systems or mixtures [2,3], and also for models described by means of a perturbation expansion [4]. The HS model is used to study the dynamical properties of fluids such as the calculation of transport and diffusion coefficients [5]. From a general point of view, this model has served for the development of research areas such as liquid crystals, granular, and soft matter, colloids and polymers, etc. One may think that the HS model is elementary, however, the system has a fascinating behavior: it has a complex phase structure (metastable states, mixing and demixing states, solid and crystalline phase, see chapter 3, Ref. [1]). Moreover, the HS system is independent of temperature (athermal). Different working groups have found a series of general state equations that attempt to represent all equilibrium conditions for this complex system [1,6,7].

A remarkable number of theoretical and simulation results has typically been calculated for the HS system in two and three dimensions [8]. A straightforward extension of the system consists of studying the properties of a gas in high dimensions, with a Euclidean metric space [5-11]. These studies are relevant not only from a theoretical perspective, since for some complex physical systems it has provided a better understanding of the equilibrium states [12-19]. For example, the average distance of a polymer in a good or poor solvent for a d -dimensional space depends on the balance between entropic and energetic interactions. De Gennes showed that the characteristic length of the equilibrium R_g (Radius of gy-

ration) depends on the effects of volume exclusion, which are proportional to the dimension of the space and the number of accessible states of the system [20]. With this in mind, it is illustrative to ask the question if it is possible to simulate a gas of hard spheres in multi-dimensional space (d -dimensions) using a standard personal computer (PC). Our results show that equilibrium states can be calculated as a function of particle density and the equation of state of gas of hard spheres for spaces of four to seven dimensions can be found, in a reasonable PC computing time (about three days for a seven-dimensional systems). The results are illustrative of how we can expand the Monte Carlo (MC) simulation algorithm to study a system in a high dimensional space. The program needs minor modifications when it is extended from 3 dimensions to a d -dimensional space.

2. Theory and simulation

The (MC) method was used in the simulation with the standard Metropoli algorithm in a microcanonical ensemble, where fixed values of the variables of energy E , number of particles N_p and volume V_d are used [8,21]. The system of hard spheres was prepared in the following form: Initially, the spheres were located in a simple d -lattice (d -box), avoiding overlapping between all the spheres. In the systems, all coordinate axes were considered perpendicular. The Euclidean distance between the centers of two spheres is

$$R = |\vec{r}_1 - \vec{r}_2| = \sqrt{x_1^1 x_1^2 + x_2^1 x_2^2 + \dots + x_d^1 x_d^2} \quad (1)$$

where d is the dimension of the space, \vec{r}_1 and \vec{r}_2 are the positions of the centers of the two spheres and $x_n^1(x_n^2)$ is the rectangular coordinate of the point $\vec{r}_1(\vec{r}_2)$. The number of

particles N_p and the size of the simulation box L_b were adjusted to the value of the particle density $\rho = N_p/(L_b)^d$. Values in the range of $N_p = 2182$ to $n_p = 16384$ were used, according to the dimension of the space and the value of the density. The thermalization of the system was performed on the first 8×10^5 steps, each step of the simulation consists of moving one particle. The construction of the histograms was performed after 7×10^5 steps. Periodic boundary conditions were taken into account in all directions, and minimum image convention for the pairwise interaction potentials was used. For the simulations, we employed a Hp workstation Z240 with intel core i7 processor at 3.8 Hz and 16 GB of memory. The MC program was extended, with small modifications, from the code of a two dimensions space to the code in d -dimensions space. The main changes are:

- The distance is calculated by adding a new coordinate, Eq. (1).
- In the initial configuration (subroutine d -box) a new loop is added for the new coordinate. Similar changes are made for the calculation of the radial distribution function, the periodic boundary conditions and minimum image convention.
- A new loop was added for the new coordinate in the part of the code that uses the Metropolis algorithm.

Appendix B shows an example of some critical changes in the program to go from two-dimensional space to a three-dimensional space. In the simulation all physical quantities are dimensionless, the dimensionless length is $L_b^* = L_b/\sigma$, the dimensionless energy is $U^* = U\beta$, the dimensionless pressure is $P^* = P\beta/\rho$, the dimensionless density is $\rho^* = \rho\sigma^d$, where $\beta = 1/k_B T$ and k_B is Boltzmann's constant and σ is the diameter of the sphere.

The equation of state of a perfect gas can be calculated explicitly in the canonical ensemble, with the definition of pressure and its connection with the partition function

$$p = k_B T \left(\frac{\partial \ln[Z_N]}{\partial V} \right)_{T,N} \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature and Z_N is the classical system's partition function [22,23]. After some algebra (appendix A), the final relation for the pressure is

$$p = k_B T \rho - \frac{\rho^2}{2d} \int_0^\infty R \frac{\partial U}{\partial R} g(R) \Omega_d dR \quad (3)$$

where $g(r)$ is the radial distribution function and Ω_d is the d -dimensional solid angle. $U(r)$ is the pairwise interaction between the particles of the system. For the system of a HS, particles have only excluded volume interactions. The potential is:

$$U(R) = \begin{cases} 0 & \text{if } R > \sigma \\ \infty & \text{if } R < \sigma \end{cases} \quad (4)$$

where σ is the diameter of the sphere. For this HS potential, the equation of state Eq. (3) is:

$$\frac{P}{\rho k_B T} = 1 + \frac{\eta}{4V_d} g(R^+) \frac{2\pi^{d/2}}{d/2 \Gamma(d/2)} \quad (5)$$

where $g(R^+)$ is the contact value ($r = \sigma/2$) of the radial distribution function, $\Gamma(x)$ is the gamma function and V_d the volume of a hypersphere:

$$V_d = \frac{\pi^{d/2} \sigma^d}{\Gamma(\frac{d}{2} + 1)} \quad (6)$$

The radial distribution function $g(r)$ is evaluated numerically in the MC simulation [8,21] by calculating the number of particles $n(r, \Delta r)$ within a spherical shell of width Δr , centered on the i particle, and at a distance r_i . A number of discrete distances r_i is sampled, and $g(r)$ is constructed as a normalized histogram. The average value is over different equilibrium configurations of the system, and normalization was taken on the total number of particles N_p and volume V_d :

$$g(r) = \frac{1}{N_p} \times \frac{\left\langle \sum_{i=1}^{N_p} n_i(r, \Delta r) \right\rangle}{\rho \Delta V_d} \quad (7)$$

The equation of state was evaluated numerically [Eq. (5)] using an extrapolation for the contact value of the radial distribution function [24] and was compared with some theoretical results proposed by various authors. The equations of state used are summarized below (for a general review see Ref. [16]). The first equation of state is a generalization of the Clausius equation that can be written by the virial expansion truncated to terms up to second order in density

$$Z_{2,0} = 1 + b_2 \eta + b_3 \eta^2 \quad (8)$$

where $\eta = \rho V_d \sigma^d$ is the packaging fraction. The values of the reduced virial coefficients b_1 and b_2 are defined as

$$b_2 = 2^{(d-1)} \quad (9)$$

$$b_3 = \frac{2^{2(d-1)} B_3}{B_2^2} \quad (10)$$

where $B_2 = 2^{d-1} V_d \sigma^d$ is the second virial coefficient and the third virial coefficient is defined by

$$\frac{B_3}{B_2^2} = 2 \frac{B_{3/4}(\frac{d}{2} + 1, \frac{1}{2})}{B(\frac{d}{2} + \frac{1}{2}, \frac{1}{2})} \quad (11)$$

with $B_x(a, b)$ the incomplete beta function and $B(a, b)$ the beta function. Another equation of state is the suggested Baus and Color with a truncated rescaled virial expansion:

$$Z_{BC} = \frac{1 + (b_2 - d)\eta + (b_3 - b_2d + d(d-1)/2)\eta^2}{(1 - \eta)^d} \quad (12)$$

A more general approach involves constructing Padé approximants from the (m, n) virial coefficients:

$$Z_{1,1} = \frac{b_2 + (b_2^2 - b_3)\eta}{b_2 - b_3\eta} \quad (13)$$

$$Z_{0,2} = (1 - b_2\eta + (b_2^2 - b_3)\eta^2)^{-1} \quad (14)$$

A rescaled Padé approach proposed by Maeo is:

$$Z_{MSAV} = \frac{1}{(1 - \eta)^d} \times \frac{b_2 - d + (d(d+1)/2 + b_2(b_2 - d) - b_3)\eta}{b_2 - d - (b_3 - b_2d + d(d-1)/2)\eta} \quad (15)$$

Finally, Song proposed using a generalization of Carnahan-Starling the following equation of state:

$$Z_{SMS} = 1 + b_2\eta \frac{1 + (b_3/b_2 - d)\eta}{(1 - \eta)^d} \quad (16)$$

All these equations of state will be compared to our MC simulations.

3. Results

In Fig. 1 we show the radial distribution function for two values of the particle density ρ and different values of the space dimension d . Figure 1(a) shows results for a density $\rho = 0.3$ and a space dimensions $d = 2, 4, 5, 7$. The structure of

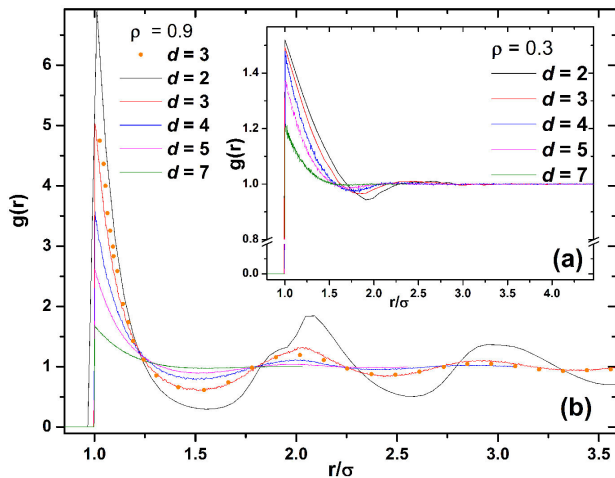


FIGURE 1. Radial distribution function for two fixed values of particle density (a) $\rho = 0.3$ and (b) $\rho = 0.9$, and different dimensional space. The continuous lines are our MC results. The orange points are an analytic solution proposed by Henderson, see the Eq. (14)-(16) in Ref. [4]. The density ρ in units of $N_p/(L_b)^d$.

the radial distribution function of the HS gas disappears as the space dimension increases. For the case of $d = 7$ (pink line) the system almost loses all its correlations and its distribution function shows a decay similar to what is observed for an ideal gas. This means that a gas of HS at small densities $\rho \lesssim 3$ behaves like an ideal gas in higher space dimensions. The configuration space of a system of HS is higher when the dimensional space is increased. Also in Fig. 1(a), it is observed that the contact values of the radial distribution function $g(R^+)$ is smaller when the space dimension increases. The pressure of a system of hard spheres decreases in a space of high dimension. Figure 1(b) shows results for a particle density $\rho = 0.9$. The $g(r)$ shows several maxima and minima that disappear when increasing the space dimension; for a value $d = 7$ (green line) the system does not show minima nor maxima and presents an exponential decay. The black line is for a system of hard disks ($d = 2$) where the $g(r)$ is highly structured. It is well known that for this density the system is in a fluid hexatic coexistence phase [25]. The orange points correspond to an analytical solution developed by, Henderson Eqs. (14) to (16) for a three-dimensional space [4]. It can be seen that our simulation (orange line) fits well with Henderson analytical solution. Similar results were obtained for other density values (not shown). It is well known that the HS gas undergoes a liquid-solid state transition for a density close to $\rho_c = 0.99$ in three-dimensional space ($d = 3$). In Fig. 1 the analysis of the radial distribution function shows, as we can expect, that for a larger spatial dimension d , the value of the critical density of the transition ρ_c also increases. In our simulations, we are limited to maximum values of $\rho = 0.9$ (higher values of ρ demand a significant number of particles, which is a severe limitation for the simulation time in our MC method). For this reason, in this work, the complete phase diagram of the hard sphere system was not explored, but in general, we can say that different space dimensions have qualitatively different phase behaviors.

In Fig. 2, we show the radial distribution function for different values of the particle density ρ with the space dimension d constant. Figure 2(a) is for a space of four dimensions $d = 4$. We can notice how increasing the particle density from $\rho = 0.3$ to $\rho = 0.9$ the structure of the gas is well-ordered, whereas for $\rho = 0.9$, (black line) the radial distribution function has several maxima and minima. Also as the density increases, the contact values of the radial distribution function cause a higher pressure [see Eq. (5)]. For a space of seven dimensions, Fig. 2-(b), we obtain comparable results with the critical difference of a less structured $g(r)$ for all densities. We can conclude, from the analysis of Figs. 1 and 2, that increasing the dimension of space creates a less structured HS gas. From Eq. (6) we note that the volume of the sphere is zero when the space dimension increases (with $\sigma = 1$), while the box of simulation is proportional to m times the size of the spheres $L_b = m\sigma$. This means that the system's translational entropy increases and its equilibrium is mostly a geometry problem.

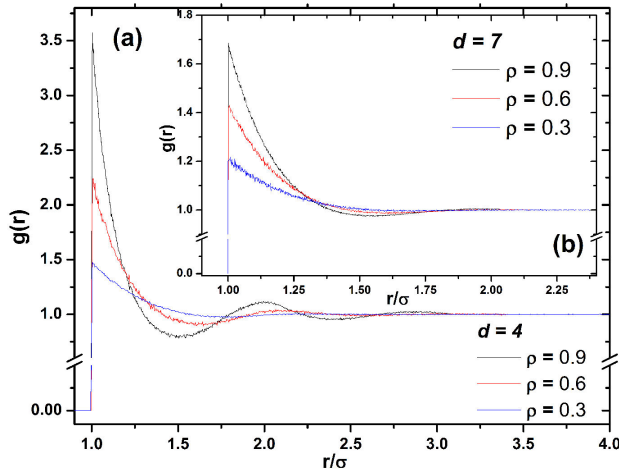


FIGURE 2. The radial distribution function. Figure (a) is for $d = 4$ and Fig. (b) is for $d = 7$, and different values of particle density ρ . Note that the vertical scale in $g(r)$ has been cut for clarity purposes. The density ρ is in units of $N_p/(L_b)^d$.

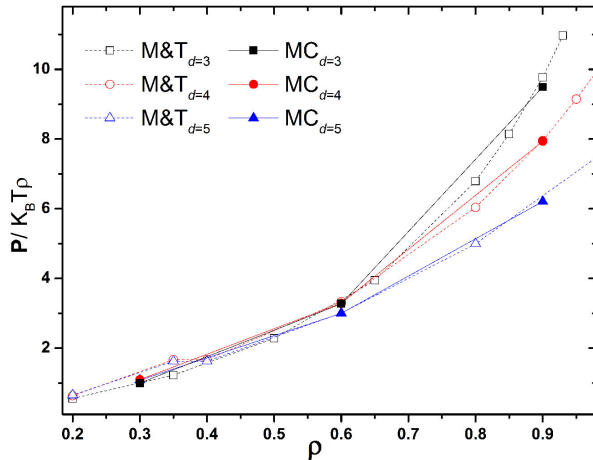


FIGURE 3. The hard sphere pressure as a function of particle density for three, four and five dimensional space. The full symbols are our MC simulations, and the open symbols are a dynamical computer simulation of Michels and Trappeniers, Ref. [5]. The density ρ in units of $N_p/(L_b)^d$.

In Fig. 3, we show the numerical pressure [see Eq. (5)] as a function of density for three different values of the Euclidean space dimension (straight line). The dotted lines are a dynamical computer simulation proposed by Michels and Trappeniers [5]. For three space dimension $d = 3, 4, 5$, the model of Michels and Trappeniers fits well with our simulation points. The Monte Carlo model of HS is capable of reproducing previous results, with the advantage that our program can be extended to study systems of higher dimensions (see Appendix B). Also, we can see in Fig. 3, that small particle densities ($\rho \lesssim 0.4$) there are not significant differences between the three numerical solutions and the space dimension. Essential differences appear when the density of particles is large ($\rho \gtrsim 0.8$). These results confirm how the entropic effects increase in spaces of high di-

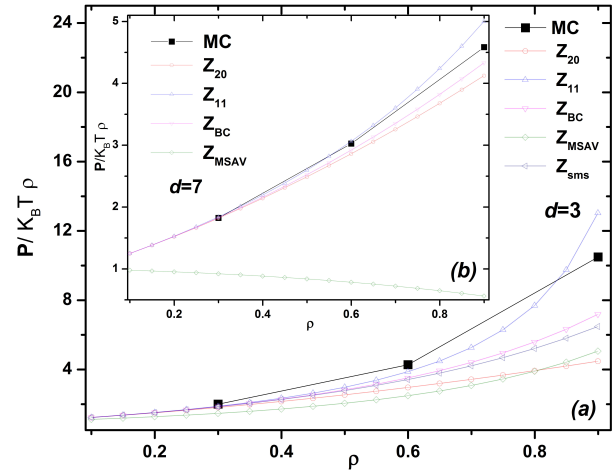


FIGURE 4. The hard sphere pressure as a function of particle density. Figure (a) is for $d = 3$ and Fig. (b) is for $d = 7$. The full symbols are our MC simulations, and the open symbols are different analytical solutions, see Sec. 2. The density ρ is in units of $N_p/(L_b)^d$.

mensions. In Fig. 4, we compared our MC simulation, for the calculation of the equation of state with some analytical results [Eqs. (8) to (16)] for the case of a three ($d = 3$, Fig. 4a) and seven ($d = 7$, Fig. 4(b)) dimensional space. At small particle densities, our MC simulation data and the theoretical results are roughly the same. When the density of particles increases the theoretical model that best fits our data is given by Eq. (16). The Z_{MSAV} model provides good results for $d = 3$ but is very bad in dimension $d = 7$. In Fig. 4(b) Z_{sms} is not shown since it is approximately equal to Z_{MSAV} for high dimensions. The intention of these simulations is not to show which of these equations of state are correct, we intend only to emphasize that the MC program used provides results of the comparable to theoretical models.

4. Conclusions

In this work, the MC simulation method was applied to study the equilibrium structure and the equation of state for a HS gas spheres. The results show that a HS gas in a space with $d < 4$ is more structured than a HS gas in high-dimensional spaces $d > 5$. The pressure of the HS system decreases as the dimension of the space increases. Our simulations fit approximately well with some theoretical results in dimensions from $d = 2$ to $d = 7$. This work did not focus on finding the critical value of the particle density ρ_c where the liquid-solid transition occurs (work in progress). The results show that with a standard personal computer, one can study complex systems in multi-dimensional spaces where, for example, new equilibrium states can be found. These phases are essential since they can correspond to a three-dimensional system, as in scaling theories for the study of equilibrium states in polymer solutions.

Appendix A

First, we find a general expression to calculate the mean value of a function F in a d -dimensional space. The mean value $\langle F \rangle$ in the canonical ensemble (T, V, N) is given by the relation

$$\langle F \rangle = \int \cdots \int P(\mathbf{R}^N) F(\mathbf{R}^N) d\mathbf{R}^N \quad (\text{A.1})$$

where $P(\mathbf{R}^N)$ is the probability density to observe a configuration and \mathbf{R} is the d -dimensional Position vector, with:

$$d\mathbf{R} = dR_1 dR_2 \cdots dR_d \quad (\text{A.2})$$

If F has a pairwise additivity functional form:

$$F(\mathbf{R}) = \sum_{i,j} f(\mathbf{R}_i, \mathbf{R}_j) \quad (i \neq j) \quad (\text{A.3})$$

then Eq. (A.1) can be written as

$$\langle F \rangle = N(N-1) \int \cdots \int P(\mathbf{R}^N) f(\mathbf{R}_1, \mathbf{R}_1) d\mathbf{R}^N \quad (\text{A.4})$$

Using the definition of the pair correlation function $\rho^{(2)}(\mathbf{R}_1, \mathbf{R}_1)$, we obtain the relation

$$\langle F \rangle = \iint \rho^{(2)}(\mathbf{R}_1, \mathbf{R}_1) f(\mathbf{R}_1, \mathbf{R}_1) d\mathbf{R}_1 d\mathbf{R}_2 \quad (\text{A.5})$$

For a system where the separation between the two particles \mathbf{R}_1 and \mathbf{R}_2 depends only on the distance $R = R_1 - R_2$ Eq. (1). Then, the integration over \mathbf{R}_1 leads to a result which is independent of \mathbf{R}_2 , hence:

$$\langle F \rangle = V_d \int \rho^{(2)}(\mathbf{R}) f(\mathbf{R}) d\mathbf{R} \quad (\text{A.6})$$

where V_d is the d -dimensional volume Eq. (6). For a system with rotational symmetry we can integrate over all the orientations, we get

$$\langle F \rangle = \rho^2 V_d \int_0^\infty g(R) f(R) R^{d-1} dR d\Omega_d \quad (\text{A.7})$$

where $\rho^2(R) = \rho g^2(R)$ is the radial distribution function and $d\Omega_d$ is the d -dimensional solid angle. Now, we calculate the pressure with Eq. (2). We only show the main results, for a detailed description see Appendix **H** in Ref. [23]. The configurational partition function Z_N is defined by:

$$Z_N = \int_{\Omega} \cdots \int_{\Omega} \exp[-\beta U_N(\mathbf{R}^N)] d\mathbf{R}^N \quad (\text{A.8})$$

Integrating on a box with sides equal $V_d^{1/d}$, we get:

$$Z_N = \int_0^{V_d^{1/d}} \cdots \int_0^{V_d^{1/d}} \exp[-\beta U_N(\mathbf{R}^N)] d\mathbf{R}_1 \cdots d\mathbf{R}_N \quad (\text{A.9})$$

with the change of variables for spatial coordinates:

$$x'_i = V_d^{-1/d} x_i \quad (\text{A.10})$$

with $i = 1, 2, \dots, d$. The integral takes the form

$$Z_N = V_d^N \int_0^1 \cdots \int_0^1 \exp[-\beta U_N(\mathbf{R}^N)] dx'_1 dx'_2 \cdots dx'_d \quad (\text{A.11})$$

To calculate the derivative of Z_N , we need to know the derivative of the potential $U_N(\mathbf{R}^N)$ with respect to the volume. Using the change of variables of the Eq. A.10 we have for the potential

$$U_N(\mathbf{R}^N) = \frac{1}{2} \sum_{i,j} U(V_d^{1/d} \mathbf{r}'_{i,j}) \quad (\text{A.12})$$

According to the metric properties of d -dimensional space:

$$\mathbf{R}_{i,j} = V_d^{1/d} \mathbf{r}'_{i,j} \quad (\text{A.13})$$

and the previous considerations, for the derivative of the potential, one can write

$$\frac{\partial U_N(\mathbf{R}^N)}{\partial V_d} = \frac{1}{2 d V_d} \sum_{i,j} \frac{\partial U_N(\mathbf{R}_{i,j})}{\partial \mathbf{R}_{i,j}} \mathbf{R}_{i,j} \quad (\text{A.14})$$

Then, we have for the pressure the following equation:

$$P = K_B T \rho - \frac{1}{2 d V_d} \iint \rho^{(2)}(\mathbf{R}_1, \mathbf{R}_1) \times \frac{\partial U_N}{\partial \mathbf{R}_{1,2}} d\mathbf{R}_1 d\mathbf{R}_2 \quad (\text{A.15})$$

finally, using the same arguments of Eq. (A.7), we have the Eq. (2).

Appendix B

In this Appendix, we show the section of the code that performs the Metropolis algorithm for a space of two-dimensions. The parts to be included for a three-dimensional system are shown as commented with the label: !-For d=3.

```

1  ! Metropolis algorithm
2  do k = 1, np
3      Call random_number(rr) ! Random Number
4      des1 = (rr-0.5)*amp
5      Call random_number(rr)
6      des2 = (rr-0.5)*amp
7  !-For d=3      Call random_number(rr)
8  !-For d=3      des3 = (rr-0.5)*amp
9
10     r1k = r1(k)
11     r2k = r2(k)
12  !-For d=3     r3k = r3(k)
13
14     r1 = r1k + des1
15     r2 = r2k + des2
16  !-For d=3     r3 = r3k + des3
17     do m = 1, np
18         if (m .ne. k) then !cond. diff. par.
19             r1 = r1
20             r2 = r2
21  !-For d=3     r3 = r3
22             rr1 = r1 - r1d(m)
23             rr2 = r2 - r2d(m)
24  !-For d=3     rr3 = r3 - r3d(m)
25             call mic (rr1,rr2,Lbox) !
26  !-For d=3     call mic (rr1,rr2,rr3,Lbox)
27             r = rr1*rr1 + rr2*rr2 ! distance eq. (1)
28  !-For d=3     r = rr1*rr1 + rr2*rr2 + rr3*rr3
29             if (r .lt. rd0) go to 1 !Pot.eq.(4)
30             endif
31         end do
32         naccept = naccept + 1 ! count
33         nacceptb = nacceptb + 1
34         r1d(k) = r1
35         r2d(k) = r2
36  !-For d=3     r3d(k) = r3
37     1 end do

```

Same as above, but to get the histogram of the radial distribution function.

```

1  ! Histogram for g(r)
2  subroutine gdr(np,Lbox,hr)
3  use coor
4  implicit real*8(A-H,O-Z)
5  real (kind=8) :: Lbox,hr
6  integer (kind=8) :: np
7  do i = 1, np-1
8      do j = i + 1,np
9          rr1 = r1(i) - r1(j)
10         rr2 = r2(i) - r2(j)
11  !-For d=3     rr3 = r3(i) - r3(j)
12         call mic (rr1,rr2,Lbox)
13  !-For d=3     call mic (rr1,rr2,rr3,Lbox)
14         r = rr1*rr1 + rr2*rr2
15  !-For d=3     r = rr1*rr1 + rr2*rr2 + rr3*rr3
16         rr = dsqrt(r)
17         if (rr .lt. Lbox/2) then
18             k = rr/hr + 1
19             gr(k) = gr(k) + 2
20         end if
21     end do
22 end do
23 end subroutine

```

Similar changes are made in other parts of the code. For a system with $d = 4$ (or 5, 6, 7) it is necessary to increase the number of coordinates. In the program, one more line is added (for each coordinate), as we do with the commented line (!-For d=3) shown above in the code.

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