

Monte Carlo para esferas duras.

Now we would like to illustrate the Monte Carlo technique in the context of a thermal problem with continuous degrees of freedom. We have chosen the hard-sphere model, since it is both simple and sufficiently important. The model has played a crucial role in the development of the statistical mechanics of fluids and solids, and as a consequence, it is a central model in condensed-matter physics.

The model approximates the interaction potential between two spherical molecules, $\phi(r)$, by:

$$\phi(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma \end{cases}$$

σ is the diameter of the hard spheres; these are termed *hard* because they cannot penetrate each other. r is the distance between the centres of mass of the two spheres. The model is an attempt to approximate the repulsive part of the interaction potential in simple systems (spherically symmetric molecules, either in reality or effectively), for instance noble gases, some metals, CH_4 , NH_3 , ... It is an *athermal* model (i.e. thermodynamic properties depend trivially on temperature) since the corresponding Boltzmann factor does not depend on temperature T :

$$e^{-\beta\phi(r)} = \begin{cases} 0, & r < \sigma \text{ (spheres overlap)} \\ 1, & r > \sigma \text{ (spheres do not overlap)} \end{cases}$$

Therefore, the only allowed configurations of N spheres are configurations where there is no overlap between the spheres; all these configurations have the same statistical weight, and possess zero energy.

Despite its ‘trivial’ appearance, the hard-sphere model contains highly non-trivial physics. The only relevant parameters are density $\rho = N/V$ and pressure p . The former is more conveniently represented by the so-called *packing fraction*, which is the ratio of volume occupied by the N spheres to total volume V . If $v = (4\pi/3) \times (\sigma/2)^3 = \pi\sigma^3/6$ is the molecular volume, then the packing fraction, η , is:

$$\eta = \frac{Nv}{V} = \rho v = \frac{\pi}{6}\rho\sigma^3$$

In terms of η , the model has (Fig. 16):

- A fluid phase in the interval $\eta \in [0, 0.494]$, with long-range positional disorder (there is, however, short-range order; this will be discussed later on).
- A crystalline phase, in the interval $\eta \in [0.545, 0.740]$, with long-range positional order. The crystal is a fcc (*face-centred cubic*) lattice. Note that the maximum possible value of the packing fraction is 0.740.

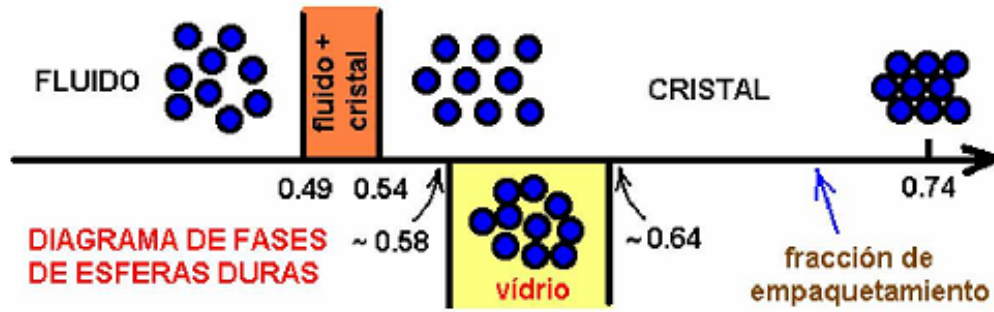


Figure 16: Phase diagram of hard spheres in terms of the packing fraction.

- An amorphous (metastable) phase, in the interval $\eta \in [0.59, 0.64]$, with long-range positional disorder but a negligible viscosity coefficient and virtually zero diffusion.

There is strongly first-order phase transition between the fluid and the crystal, at a reduced pressure $p^* \equiv p\sigma^3/kT \simeq 8.9$

Before presenting the Monte Carlo algorithm as implemented for hard spheres, we introduce a method to calculate the pressure, along with two simple theories, applicable to the fluid and the crystal, respectively, that describe in simple (albeit approximate) terms the *equation of state* of the system, i.e. the function $p(\rho)$. In the theory for the crystal phase calculations are most easily done using the (unweighted, i.e. uniform sampling) Monte Carlo integration technique; in the former, it may also be necessary to use it in case refinements be required.

- **Pressure and radial distribution function.** The radial distribution function $g(r)$ is a function of the distance between a pair of particles. It is a measure of the local order of the fluid. In practice it is computed as the mean number of particles around a given one at distance r , divided by the expected number should interactions be turned off (the latter is just the bulk density ρ). For a dense fluid, the function shows a strong first peak at distances $\sim \sigma$, and a damped oscillatory structure tending to one as r increases. As the density is increased, this structure becomes more and more sharpened. Knowledge of $g(r)$ for a fluid allows different thermodynamic properties to be computed. For example, the reduced pressure is given by

$$\frac{p}{\rho kT} = 1 - \frac{2\pi\rho}{3kT} \int_0^\infty dr r^3 \phi'(r) g(r) \quad (6)$$

where $\phi'(r)$ is a derivative with respect to r . This is valid for any spherically symmetric interaction potential. In particular, for the hard-sphere potential (where $\phi'(r)$ exhibits delta-type behaviour at $r = \sigma$), the above expression can be written in terms of the value of $g(r)$ at $r = \sigma$ (the so-called *contact value*):

$$\frac{p}{\rho kT} = 1 + \frac{2\pi\rho}{3} \sigma^3 g(\sigma^+)$$

In the simulation, $g(r)$ is computed as a histogram; we will explain this later.

- **Clausius equation of state for the fluid.** We start from the ideal-gas equation of state, which we know is exact in the low-density limit $\rho = N/V \rightarrow 0$:

$$pV = NkT$$

Here p is the pressure, V the volume, N the number of particles, k Boltzmann constant, and T the temperature. At higher density the volume occupied by the spheres has to be taken into account, and the equation must be modified as

$$p(V - Nb) = NkT \quad \rightarrow \quad p = \frac{NkT}{V - Nb}$$

where b is the *excluded volume per particle*. This volume arises from the fact that each sphere has an associated volume within which the centres of mass of other spheres are not allowed. Every pair of spheres contributes to this volume with

$$b = \frac{1}{2} \times \left(\frac{4\pi}{3} \sigma^3 \right) = \frac{2\pi}{3} \sigma^3 = 4v$$

Then:

$$\frac{pV}{NkT} = \frac{1}{1 - Nb/V} = \frac{1}{1 - 4\eta}$$

which is *Clausius equation*. This equation predicts the following virial expansion:

$$\frac{pV}{NkT} = \frac{1}{1 - 4\eta} = 1 + 4\eta + 16\eta^2 + \dots$$

The coefficient of the term η^2 is incorrect; actually its correct value is 10. The predicted higher-order coefficients are also in error. In fact, the virial coefficients, $B_n^* = B_n/v^{n-1}$, defined by the virial expansion

$$\frac{pV}{NkT} = 1 + \sum_{n=1}^{\infty} B_{n+1} \rho^n = \sum_{n=1}^{\infty} B_{n+1}^* \eta^n$$

can be obtained from Clausius equation as $B_n^* = 4^n$; scaling with the second virial coefficient, we get

$$\frac{B_n}{B_2^{n-1}} = 1, \quad \forall n > 1$$

which is a very gross approximation. In particular, Clausius equation predicts a divergence of the pressure at a packing fraction $\eta = 1/4 = 0.250$, which is clearly wrong since we know that the fluid is stable at least up to $\eta = 0.494$. Clausius equation is approximate, and can be used only at low densities.

The free energy can be obtained from the pressure by integration; the final result is

$$\frac{F}{NkT} = \log \left(\frac{\rho \Lambda^3}{1 - 4\eta} \right) - 1 \quad (7)$$

Clausius equation can be improved in various ways. Much effort has been devoted over the last decades to this goal. A typical approach incorporates knowledge of

higher-order virial coefficients to build up a more accurate equation of state. One of these approaches leads to the so-called *Carnahan-Starling* equation of state which, when properly integrated in density, gives the following free energy per particle:

$$\frac{F}{NkT} = \log(\rho\Lambda^3) - 1 + \frac{(4-3\eta)\eta}{(1-\eta)^2} \quad (8)$$

A more general approach involves constructing Padé approximants. For example, if the first two virial coefficients, B_2 and B_3 , were known, the coefficients a_1 and a_2 in the following Padé approximant,

$$\frac{pV}{NkT} = \frac{1 + a_1\rho + a_2\rho^2}{1 - \rho v} = 1 + B_2\rho + B_3\rho^2 + \dots$$

can be easily obtained. The approximant is only adjusted for low densities, but its functional form is expected to be valid for a much larger density range.

Expressions for the virial coefficients, based on statistical mechanics, can be written. They include the so-called *Mayer function*, $f(r) = \exp[-\beta\phi(r)] - 1$. The first two coefficients read:

$$\begin{aligned} B_2 &= -\frac{1}{2} \int d\mathbf{r} f(r) \\ B_3 &= -\frac{1}{3} \int d\mathbf{r} \int d\mathbf{r}' f(r) f(r') f(|\mathbf{r} - \mathbf{r}'|) \end{aligned} \quad (9)$$

Expressions for the higher-order coefficients are considerably more complicated. For hard spheres, the first three coefficients are known exactly:

$$\begin{aligned} B_2 &= \frac{1}{2} \int d\mathbf{r} \Theta(\sigma - r) = 2\pi \int_0^\sigma dr r^2 = \frac{2\pi}{3} \sigma^3 = 4v \\ B_3 &= \frac{5\pi^2}{18} \sigma^6 \simeq 2.74156 \\ B_4 &= \left[-\frac{89}{280} + \frac{219\sqrt{2}}{2240\pi} + \frac{4131}{2240\pi} \arccos\left(\frac{1}{\sqrt{3}}\right) \right] B_2^3 \end{aligned} \quad (10)$$

The higher-order coefficients, B_n with $n > 4$, must be calculated numerically. Note, in passing, that Clausius' equation predicts $B_3 = 16v^2 = 16 \times (\pi\sigma^3/6)^2 = 4.3865$, to be compared with the exact value 2.7416; not a fair comparison really!

As an example of how the higher-order virial coefficients can be evaluated numerically, let us evaluate the B_3 coefficient (which, as mentioned, is known exactly) using a technique based on the multidimensional Monte Carlo integration. We use Eqn. (9), which extends over all space, but only when three spheres overlap at the same time does the integrand contribute. In spherical coordinates:

$$\begin{aligned} B_3 &= -\frac{1}{3} \times \int_0^\sigma dr r^2 \int_{-1}^1 d(\cos\theta) \int_0^{2\pi} d\phi \\ &\quad \times \int_0^\sigma dr' r'^2 \int_{-1}^1 d(\cos\theta') \int_0^{2\pi} d\phi' f(r) f(r') f(|\mathbf{r} - \mathbf{r}'|) \end{aligned}$$

M	B_3^{MC}	$B_3^{\text{MC}}/B_3^{\text{exact}}$
10^2	2.51933	0.91894
10^3	2.65935	0.97002
10^4	2.77402	1.01184
10^5	2.74633	1.00174
10^6	2.74411	1.00093
10^7	2.74242	1.00032
10^8	2.74170	1.00005

Table 1: Third virial coefficient as obtained from the Monte Carlo integration method for different number of configurations generated, M , and ratio to the exact value, given by Eqn. (10).

Note that the jacobians in θ coordinates have been absorbed into differentials, so that it is $\cos \theta$ that is to be sampled uniformly. Let us place a sphere at the origin, and choose a location for a second sphere randomly so that it overlaps with the first. This is easily done if we randomly and uniformly generate numbers $(r, \cos \theta, \phi)$ in the intervals $[0, \sigma] \times [-1, 1] \times [0, 2\pi]$. Then, one of the Mayer functions, say $f(r)$, is always equal to minus one. If we do the same for a third sphere, i.e. randomly generate a position so that it always overlaps with the first, we have $f(r') = -1$. Now there would remain to check whether the second and third spheres overlap, i.e. whether the value of the Mayer function $f(|\mathbf{r} - \mathbf{r}'|)$ is 0 or -1 . The approximation based on Monte Carlo integration would, in this case, be

$$B_3 = \frac{1}{3} \times \frac{1}{M} [(\sigma) \times (2) \times (2\pi)]^2 \sum_{i=1}^M r_i^2 r_i'^2 \xi_i = \frac{(4\pi\sigma)^2}{3M} \sum_{i=1}^M r_i^2 r_i'^2 \xi_i$$

where $i = 1, \dots, M$ is a Monte Carlo step (which includes sampling two spheres within the excluded volumen of the central one) and $\xi = 1$ or 0 depending on whether the two spheres overlap. Table 1 contains results obtained with different number of MC steps generated. As can be seen, the results for B_3 converge nicely to the exact value. This technique is obviously useful beyond the fourth virial coefficient, for which there are no exact results.

- **Free-volume equation for the crystalline phase.** For the other stable phase, the crystal, a simple approximation, called *free-volume approximation*, can be made. Let us consider a crystalline lattice, with the spheres vibrating about their equilibrium positions, which coincide with the sites of the lattice. The free-volume approximation assumes the neighbours of a given sphere to be fixed in their equilibrium positions, and that our central sphere moves in the ‘cage’ left by the neighbours. The problem is then that of an ideal particle in an external potential; the latter is infinite whenever the particle overlaps with the neighbours, and zero otherwise. This gives rise to a *free volume*, v_f , and the partition function of the particle will be $z = v_f$. The partition function for the N spheres (which we assume to be distinguishable,

since a particular sphere has to be chosen to calculate v_f) will be

$$Z = \frac{1}{h^{3N}} \prod_{i=1}^N \int_{v_f} d\mathbf{r}_i \int d\mathbf{p}_i = \frac{v_f^N}{\Lambda^{3N}}$$

where Λ is the thermal wavelength (this comes from the integration over momenta). The free energy will be:

$$F = -kT \log Z = -NkT \log \left(\frac{v_f}{\Lambda^3} \right), \quad \frac{F}{NkT} = \log \left(\frac{\Lambda^3}{v_f} \right)$$

and the pressure:

$$p = - \left(\frac{\partial F}{\partial V} \right)$$

The dependence of F on V (or density ρ) comes through v_f , which depends on how close or how far the neighbours of the central sphere are, which in turn depends on density.

To calculate v_f we can make approximations, or we can use the Monte Carlo integration method, in the same manner as we used it to compute the third virial coefficient B_3 . In Fig. 17 the situation is explained on a triangular lattice. Six neighbours of a central sphere (the latter is not shown) are depicted in light grey. The region where the centre of mass of the central particle could be located without ever overlapping with its neighbours is also depicted (the region is bounded by circular sectors, each centred on each of the six neighbours and with radius 2σ). On a two-dimensional triangular lattice the free volume v_f can be obtained analytically. The three-dimensional case requires considerably more effort, so that Monte Carlo integration is well suited to the problem: we would generate positions for the central particle within a volume W that contained the volume v_f we want to calculate; any point generated such that there is overlap with any of the neighbouring spheres is rejected (or given zero weight). The free volume would be:

$$v_f \simeq \frac{W}{M} \sum_{m=1}^M \xi_i, \quad \xi_i = \begin{cases} 1, & \text{no overlap} \\ 0 & \text{overlap} \end{cases}$$

We have to make sure that the volume W is sufficiently large as to include the free volume. The quantity ξ_i is easily calculated by simply generating the positions of the n nearest neighbours of the lattice in question. For example, for the fcc lattice $n = 12$, and their positions are given by:

$$\left(\pm \frac{a}{2}, \pm \frac{a}{2}, 0 \right), \quad \left(\pm \frac{a}{2}, 0, \pm \frac{a}{2} \right), \quad \left(0, \pm \frac{a}{2}, \pm \frac{a}{2} \right)$$

where a is the lattice constant (related to density by $\rho = 4/a^3$). This model, among other things, explains why the stable crystalline phase is a fcc lattice and not, for example, the bcc *body-centred cubic* lattice.

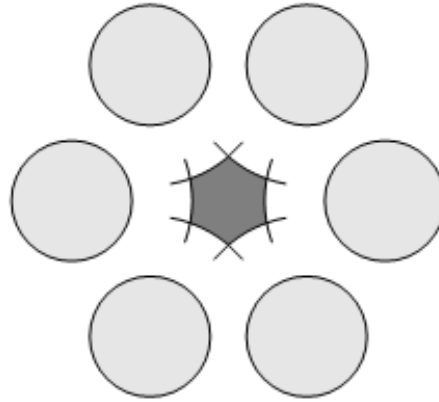


Figure 17: The six neighbours of a central sphere (the latter is not shown) depicted in light grey. The region where the centre of mass of the central particle could be located without ever overlapping with its neighbours is also depicted.

- Phase transition between a fluid and a crystal in hard spheres.** Fig. 18 shows the free energies of the fluid and two crystal structures for the hard-sphere system. The first one is obtained from the Carnahan-Starling approximation, whereas the latter two were obtained using the free-volume approach. Note that the fcc phase is always more stable than the bcc phase, which is metastable (actually computer simulations have proved it to be unstable against shear modes, not considered in the simple free-volume approach). Also note that the fluid branch has been computed even for high densities, for which the fluid no longer exists (this could be considered as a 'highly metastable' fluid). The fluid and fcc curves intersect at some density. This demonstrates the fluid-to-solid transition is of first order. In order to obtain the densities (or packing fractions) of the coexisting fluid and crystal phases, we would have to apply a common-tangent construction, i.e. obtain ρ_f and ρ_c for fluid and crystal by solving the equations $p_f = p_c$ and $\mu_f = \mu_c$ simultaneously (μ is the chemical potential). Results from Monte Carlo estimations of free energies give the following values for the coexistence densities: $\rho_f \sigma^3 = 0.943$ and $\rho_c \sigma^3 = 1.041$, which correspond to packing fractions $\eta_f = 0.494$ and $\eta_c = 0.545$.

• Monte Carlo code for thermal simulation of hard spheres

This FORTRAN code implements the MC simulation of thermal averages for the hard-sphere system using the importance-sampling technique. The code performs the MC dynamics, and calculates the radial distribution function from which, in a (separate) final calculation, the pressure is evaluated. The results of the simulations obtained with this code can be compared with the approximate equations of state for fluid and crystal phases obtained in the previous sections. Before presenting the code we will digress a little on the peculiarities of the Monte Carlo algorithm for the system of hard spheres.

In Section 2 we presented the Metropolis et al. algorithm, and extended it to more than one random variable. In the case of N hard spheres contained in a rectangular box, a move consists of randomly moving a sphere and checking whether this displacement gives an overlap or not (Fig. 19). If there is no overlap, the move is accepted; otherwise it is rejected. This is so because the acceptance probability in this case is simply

$$e^{-\beta\Delta E} = \begin{cases} 0, & \text{there is at least one overlap} \\ 1, & \text{there are no overlaps} \end{cases}$$

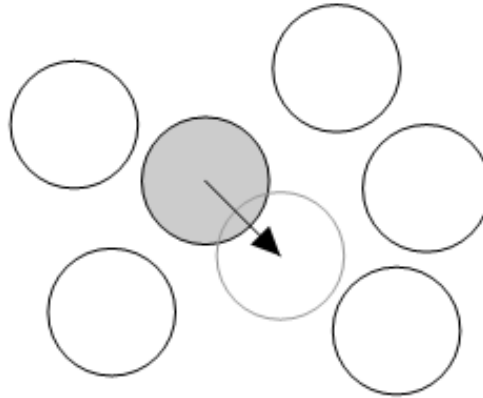


Figure 19: The chosen sphere (in gray) is given a random displacement to a test position (in gray line). The neighbouring spheres are represented as circles in black line. In this case the displacement results in no overlap, and the move will be accepted.

The algorithm is then as follows:

1. We prepare an initial (non-overlapping) configuration for the N spheres within the rectangular box, at the density we wish to investigate (a high-density

disordered configuration is difficult to obtain; that is why normally we will start from a perfectly ordered configuration, even if the density is too low for the crystal phase to be stable).

2. We choose a sphere, at random or sequentially, and displace it by a random amount (within some distance ζ from the original position)
3. We check for overlaps with neighbouring spheres. If there is at least one overlap, the move is rejected; if there are no overlaps, the move is accepted.
4. We repeat the process until the N spheres have been visited (or N moves have been performed). Then we will have completed one MC step.
5. We iterate the procedure as many times as needed

As in any implementation of the Metropolis et al. algorithm, an initial warm-up period is required before taken averages. Also, the ratio of accepted moves to total moves should be chosen to be about 0.5, and this is realised by adjusting the value of the maximum displacement ζ (clearly, if ζ is too large moves will mostly result in overlaps, and most moves will be rejected, while if ζ is very small the moves will almost always be accepted).

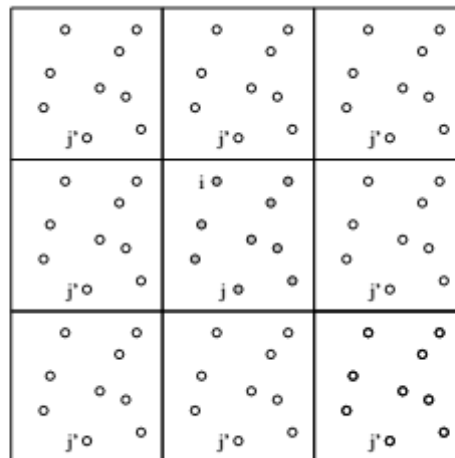


Figure 20: Central simulation box surrounded by replicas (in the case of two-dimensional systems and square boxes there are 8 replicas; for three-dimensional systems there are 27 replicas). Particles in the replicas have the same positions and velocities as in the central box; then, when exiting one box they supersede their *clone* that, in turn, is exiting its box (periodic boundary conditions). Distance between the i th and j th particles is calculated as the minimum distance between the i th and all the clones of the j th particles, named j' in the figure (minimum image convention). In the example, the minimum distance corresponds to one of the clones of j (the one right above the central box), not to j itself.

There are some technicalities of the method that we discuss in the following.

- a. Periodic boundary conditions.
When simulating extended (bulk) systems it is convenient to use periodic

boundary conditions (Fig. 20). These boundary conditions minimise the effects of surfaces on the results, and consist of placing replicas or images of the system next to it and along all directions. Let L_x, L_y, L_z be the sides of the (rectangular) simulation box. In practice, the method redefines the coordinates of any particle that gets outside of the box; for example, if at some instant of time the x coordinate of a particle is $x > L_x$, then we make $x - L_x \rightarrow x$. If $x < 0$, then we redefine $x + L_x \rightarrow x$. This is done on every coordinate of every particle along the simulation.

→ b. Minimum image convention.

For pair-wise interaction potentials, we have to calculate the distance between the two particles of a given pair. For rectangular simulation boxes the simulation box has 26 replicas. This means that, when calculating the distance between the i -th and the j -th particles, one has to decide which of the 27 possible distances between the i -th particle and the j -th particles, including itself *and its 26 replicas*, has to be taken into account, since all or some of them can be within the interaction range. The minimum image convention chooses the one which gives the least distance $|\mathbf{r}_j - \mathbf{r}_i|$ (Fig. 20). See the code for a possible algorithm that implements this.

→ c. Calculation of radial distribution function.

We focus on a particular sphere. Then $g(r)d^3r$ is the number of particles to be found in a differential volume element d^3r a distance r from that sphere, with respect to the number that would obtain should interactions between particles be turned off (or equivalently, with respect to the corresponding number that would obtain very far from the sphere, where interactions –and for that matter correlations– are zero or negligible). In practice, given the expected spherical symmetry of the problem, we consider a spherical differential volume element of width Δr around a particular particle i (see Fig. 21). Put in a mathematical expression:

$$g(r) = \frac{1}{N} \times \frac{\left\langle \sum_{i=1}^N n_i(r, \Delta r) \right\rangle}{4\pi r^2 \rho \Delta r}$$

The average $\langle \dots \rangle$ is over different configurations of the spheres. Note that an average over particles is also explicit in the expression (sum over particles, $i = 1, 2, \dots, N$) and division by N ; this can (and should) be done, as all particles are equivalent and it helps improve the accuracy. $n_i(r, \Delta r)$ is the number of particles within a spherical shell of width Δr , centred on the i -th particle, and at a distance r from this particle. This can be easily computed for any given configurations of sphere. Finally, $4\pi r^2 \Delta r$ is the volume of such a spherical shell, which can also be approximated by

$$\frac{4\pi}{3} \left[\left(r + \frac{\Delta r}{2} \right)^3 - \left(r - \frac{\Delta r}{2} \right)^3 \right]$$

When multiplied by ρ , we get the number of particles within the volume at very large distance (rigorously speaking, we have to multiply by $(N-1)/V$, not by $\rho = N/V$, since the central particle cannot be counted). Then, for

large r , the ratio should tend to unity. In the simulation a number of discrete distances r_i is sampled, and $g(r)$ is constructed as a normalized histogram.

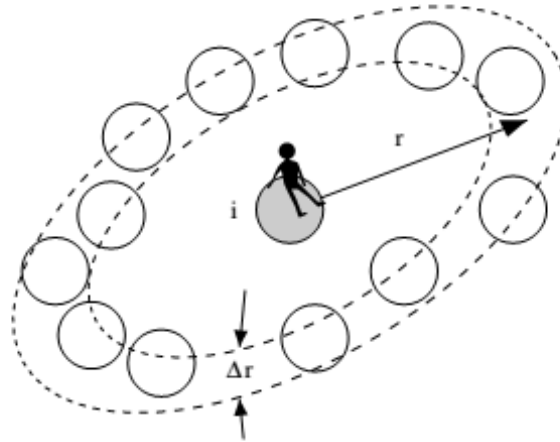


Figure 21: The radial distribution function at distance r is calculated by counting the number of particles in a spherical shell of radius r (here represented by a ring) and thickness Δr when the origin is at the i th particle, giving $n_i(r, \Delta r)$. This is done for all the N particles and then averaged (dividing by N). The resulting quantity is normalised to the number of particles expected in the shell if there were no interactions, i.e. $4\pi r^2 \Delta r \rho$.