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Incorporation of the intensive and extensive entropy contributions in the disk intersection theory of a hard disk system

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The one-body free volume, which determines the entropy of a hard disk system, has extensive (cavity) and intensive (cell) contributions. So far these contributions have not been unified and considered separately. The presented theory incorporates both contributions, and their sum is shown to determine the free volume and partition function. The approach is based on multiple intersections of the circles concentric with the disks but of twice larger radius. The result is exact formulae for the extensive and intensive entropy contributions in terms of the intersections of just two, three, four, and five circles. The method has an important advantage for applications in numerical simulations: the formulae enable one to convert the disk coordinates into the entropy contribution directly without any additional geometric construction. The theory can be straightforwardly applied to a system of hard spheres.

Key words: *hard discs, free volume, partition function, intersections*

1. Introduction

Spheres and their arrangement in space have been playing a very notable role in practical life and, in particular, in mathematics and physics. Recently Maryna Vjazovska received the Fields Medal for solving the problem of dense hard sphere packing in 8 [1] and 24 [2] dimensions. In physics, however, the analytical achievements are more modest. In statistical physics we are interested in a random packing problem of hard spheres in a macroscopic volume. Over more than a century, the idea to model molecules as hard spheres has been widely used in the theory of liquids [3–5]. The model of spheres, interacting only by their hard cores, plays the role similar to that of Ising's model in the theory of magnetism, but despite apparent simplicity, the behavior of hard sphere systems is so complex mathematically that no exact analytical result has been obtained in the physical dimensions 3 and 2. Under these circumstances, the numerical Monte Carlo and molecular dynamics approaches have become the main tools in the study of 3D hard sphere and 2D hard disk (HD) systems (see review [6] and numerous references therein). However, even using the modern powerful numerical methods one encounters the fundamental theoretical problem of computing the main thermodynamic potential of hard sphere and HD systems, the entropy. Although the problem of hard spheres is very similar to that of HDs, for simplicity, in this paper the presentation will be mainly related to HDs.

The potential energy of a HD system is zero and the entropy provides the total thermodynamic information and, in particular, equation of state and possible subtleties of the phase behavior as a function of density which is the single parameter of the system state. The numerical simulations consist in producing different independent configurations of the coordinates of the disks which is the task input, and then certain related theory must provide calculation of the entropy, equation of state, and other quantities of interest which are the task outcome. In principle, the ultimate theory must give the outcome directly from the coordinates of the disks (with the consequent averaging over different configurations), but actually the available theoretical methods relate the coordinates of the disk with the expected outcome only through intermediate and quite sophisticated geometrical constructions. The main elements of such constructions are the so-called free volume, cavity, "private" one-disk cell, and the surface thereof. For a brief review and to present the main idea of this paper, we first introduce these quantities.

A HD of radius $\sigma/2$, the core, is supplemented with a concentric circle of radius σ which is called here σ circle. The cores cannot overlap, but their σ circles can overlap and are transparent for cores. A configuration of N HDs in a 2D volume V consists of N nonoverlapping cores and N connected σ circles which can overlap, figure 1. The *free volume* V_N of a disk in a given configuration of an *equilibrium* N *HD system* is the volume accessible for its center in this configuration, which is the total V minus union of the rest $N-1$ σ circles; V_N can comprise more than one disconnected piece (in figure 1, a single piece is shown). The *cavity* C_N *in a HD system of* N *HDs* is the area where an additional HD can be inserted which is total V minus *union of all* N σ *circles*. The private cell c_N of a disk *in a HD system of* N *HDs* is the free volume of this disk V_N without the cavity C_N (stroked area, figure 1); if the cavity is zero and no additional HD can be inserted, then private cell is the total free volume of the disk. The free volume, cavity, and private cell in the case of a single free area are illustrated in figure 1. It is seen that the division on cavity and private cell of the dashed disk depends on the position of this disk, but the total free volume $V_N = C_N + c_N$ does not depend on its coordinate. The average free volume $\langle V_N\rangle_N$, average cavity $\langle C_N\rangle_N$, and average private cell per disk $\langle c_N\rangle_N$ are those for a single configuration of N disks averaged over the configurations of the *equilibrium system of the same N disks.* The perimeters (surfaces in 3D) of all the three volumes introduced are complex lines (surfaces) whose shapes and lengths are not in a one-to-one relation with the volume size. In the above definition, we emphasized that the quantities related to an N disk system are defined for the equilibrium system of the same N disks.

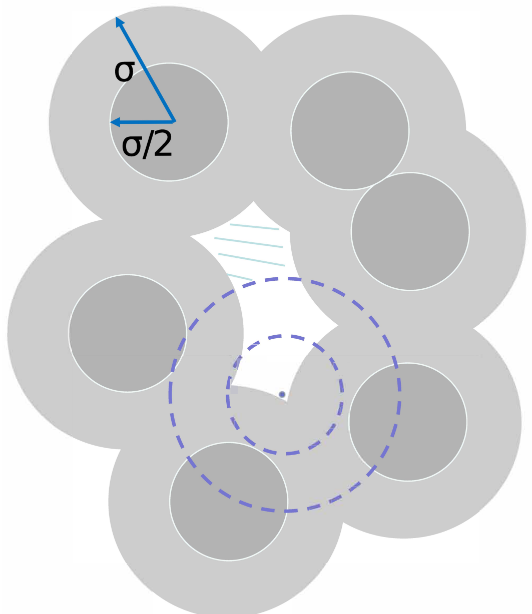

Figure 1. (Colour online) Fragment of a system of N HDs. The $N-1$ HDs of radius $\sigma/2$ are represented by dark circles and the connected concentric σ circles by light circles. The N-th disk and circle are shown by dashes. The white area in between is the free volume of N-th disk since its center can be anywhere in this area. Only the stroked fraction of the white area is the cavity in the N HD system. The clear fraction of the white area is not cavity, but is available for the center of dashed disk center. This clear white area is equal to the area of dashed σ circle, $\pi\sigma^2$, minus its fraction overlapped by other σ circles.

In 1977 Speedy introduced the spare volume and defined it as follows: "The spare volume V_s of an assembly of N spheres of diameter σ in a volume V is defined as the average over configurations of the volume which is not within σ of a sphere center, . . . , the probability that another sphere can be placed at a random point in the assembly” [7]. Clearly, this is equivalent to a cavity available for an additional, $N+1$ disk in a system of N disks, and which is averaged over configurations of N HDs. As a result, Speedy related the partition function (PF) of a HD system with the product of cavities $\langle C_{N'}\rangle_{N'-1}$ in the systems of a number of disks reduced by one, i.e., of $N-1$, $N-2, \ldots, 1, 0$ disks, which are averaged over the equilibrium systems of respectively $N-1$, $N-2, \ldots, 1, 0$ disks in the same volume V [7]. The way this PF was obtained was going back to the earlier results by Adams [8] and Andrews [9] which had in turn been inspired by Widom’s approach [10]. But Speedy was the first to address the calculation of the spare volume in a HD system in terms of intersections of the disks [11] which has greatly influenced the further development of this area [12]. Later Speedy explicitly shifted from the nomenclature of spare volumes to cavities [11].

Actually, however, the formula for the PF has not been further employed. Instead, in 1980 Speedy proposed the equation of state which relates the pressure with the ratio (average cavity volume)/(average cavity surface area) [11, 13]. Since then different geometrical methods of finding the cavities and their surface have become the main emphasis in the ongoing studies of hard particle systems [14–21]. However, the complex shape and connectedness of cavity space makes it very difficult to perform precise measurements of the quantities characterizing them, which resulted in new and new geometrical constructions that are highly nontrivial to implement [14–16, 19, 20]. The main problem of this approach is that, even for densities far from the crystallization density, cavities become so rare that finding them was sometimes called a task futile [16]. The root of this problem is that a cavity in an N HD system has been mainly computed as that of N-th disk in an equilibrium system of $N-1$ HDs. However, while in an equilibrium system of N HDs the place for N-th disk is ensured, in a dense equilibrium system of $N-1$ HDs, a place for an additional N-th disk is a very rare event. The paradox is that relating the cavity with a system of a smaller number of disks when considering an N disk system, one finds no place for N-th disk. This problem was pointed out by Schindler and Maggs who had to invent a modified numerical algorithm for finding the cavities and distinguishing them from free volumes [20].

The cavity is an extensive quantity that scales with the number of disks and volume. At the same time, even when an additional, $N+1$ disk cannot be inserted, the original N disks can vibrate in their cages created by their neighbors. This implies that the total entropy is nonzero and the volumes of such cages are its source even in the absence of cavities which is the case of densities approaching that of crystallization. These cages are what is called private disk cells in the cell models [22–25]. Even before Speedy’s publication [7], Hoover and coworkers [22–24] correctly argued that along with the extensive cavity volume, there must be an intensive one which scales as V/N and consists of individual single-disk cells. The free volume is the sum of these two terms, and when the cavity is getting smaller and smaller, the total free volume reduces to the volume of individual cells. Based on this important idea, as early as in 1972, Hoover, Ashurst, and Groover showed that the pressure can be expressed via the average ratio of the *free volume* to its surface which incorporates the cell contribution [23]. The cell model can quantitatively describe the HD equation of state near the freezing density in numerical simulations [22–24] and even allows one to obtain qualitatively accurate results analytically [25]. The cell models also have the problem of describing the cell distribution with a strong geometric component, but the main problem is to connect the one-body cell approach with a many-body one, i.e., to incorporate the intensive and extensive free volumes and entropy contributions in a unified theory.

In this paper we present such a theory in which the extensive and intensive terms have the same status and are computed in the framework of the same approach. We develop the method of multiple intersections of σ circles and, in terms of their intersection volumes, express the free volume, its extensive and intensive parts, and the PF of a system of N HDs. Due to the fact that only up to five σ circles can intersect without overlapping of their cores, the theory needs only four quantities, i.e., the intersection volumes of two, three, four, and five σ circles. These four quantities are fully specified by the disks coordinates and can be calculated analytically using the formulae obtained in [26–28]. The theory does not resort to a system of reduced number of HDs and gives the values of a cavity, private cell, and total free volume in a system of N HDs only in terms of this very N HD system. No geometrical or any other intermediate constructions appear between the input, coordinates of the disks, and the output, quantities of interest, and the only source of inaccuracy is that of the numerical simulations.

The paper is organized as follows. In section 2, the method of multiple disk intersections is introduced and the general formula for the free volume of a single disk is derived. Section 3 is devoted to the connection between the single disk volume and many-body description. First Speedy-Widom's approach is used to derive the PF. It is shown that this PF is exactly Speedy's PF [11] in the form of a product of cavities in the equilibrium systems of the reduced number of disks. Next it is shown that, in the thermodynamic limit, the correct PF is the product of the free volumes averaged in the proper systems. In section 4, the formulae relating the extensive and intensive free volume contributions with intersections of σ circles are obtained and their application to the average values is explained. In section 5, the analytical computation of all the intersections of σ circles and the intensive and extensive terms for the densely packed triangular HD lattice is presented in detail. It shows that both terms in this state vanish identically. Final section 6 is a brief conclusion.

2. Hard disk interaction and multiple disk intersections

The configuration PF of a 2D system of N particles in the 2D volume V with paiwise interaction U_{ij} is the following integral:

$$\begin{aligned} Z_N &= \int\limits_V \mathrm{d}x^N \exp\Bigg(-\frac{1}{2}\sum_{i,j=1}^{N} U_{ij}\Bigg) \\ &= \int\limits_V \mathrm{d}x^{N-1} \exp\Bigg(-\frac{1}{2}\sum_{i,j=1}^{N-1} U_{ij}\Bigg)\int\limits_V \mathrm{d}x_N \exp\Bigg(-\frac{1}{2}\sum_{i=1}^{N-1} U_{Ni}\Bigg), \end{aligned} \tag{2.1}$$

where x_i are the two component vectors of coordinates of the disks, $\mathrm{d}x^N = \mathrm{d}x_1 \ldots \mathrm{d}x_N$, and we separated the x_N integral. For HDs of the radius $\sigma/2$, the potential $U_{ij} = \infty$ for x_j within the circle of radius σ centered at x_i, and $U_{ij} = 0$ for x_j outside this circle. We introduce a circle B_i, $i = 1, \ldots, N-1$:

$$B_i = \{x_N : |x_i - x_N| \leqslant \sigma\}. \tag{2.2}$$

By definition, the indicator $\tau_i(B_i)$ of the set of points $x_N \in B_i$ is

$$\tau_i = \tau(B_i) = \begin{cases} 1, & x_N \in B_i, \\ 0, & x_N \notin B_i. \end{cases} \tag{2.3}$$

The product of n indicators of n different sets is the indicator of the intersection set shared by all of them. Such product of two indicators, which is nonzero only if the two related circles intersect, can be defined as

$$\tau_{tj} = \tau_i\tau_j = \begin{cases} 1, & x_N \in B_i \cap B_j, \\ 0, & x_N \notin B_i \cap B_j, \\ 0, & B_i \cap B_j = \varnothing. \end{cases} \tag{2.4}$$

Then, by definition,

$$\begin{aligned} \tau_{i_1\ldots i_n} &= \tau\bigcap_{k=1}^{n} B_{i_k} \\ &= \begin{cases} 1, & x_N \in \bigcap\limits_{k=1}^{n} B_{i_k}, \\ 0, & x_N \notin \bigcap\limits_{k=1}^{n} B_{i_k}, \\ 0, & \bigcap\limits_{k=1}^{n} B_{i_k} = \varnothing, \end{cases} \end{aligned} \tag{2.5}$$

where $\bigcap_{k=1}^{n} B_{i_k}$ is the set of points x_N shared by all circles B_i, i.e., their intersection.

Now, the utmost right exponential in Z_N (2.1) for the HD interaction can be presented in terms of τ's. It is easy to see that the HD interaction is equivalent to the following formula:

$$\mathrm{e}^{-U_{Ni}/2} = 1 - \tau_i. \tag{2.6}$$

This formula shows that the center of disk $N \neq i$ cannot enter the circle B_i centered at x_i which has the radius σ twice the HD radius $\sigma/2$. The product of two exponentials is

$$\mathrm{e}^{-(U_{Ni}+U_{Nj})/2} = (1-\tau_i)(1-\tau_j). \tag{2.7}$$

Similarly,

$$\begin{aligned}\exp\left(-\frac{1}{2}\sum_{i=1}^{N-1} U_{Ni}\right) &= \prod_{i=1}^{N-1}(1-\tau_i)\\ &= 1-\sum_{i=1}^{N-1}\tau_i + \sum_{i>j}^{N-1}\tau_i\tau_j - \sum_{i>j>k}^{N-1}\tau_i\tau_j\tau_k + \dots + (-1)^{N-1}\sum_{i_1>i_2>\dots>i_{N-1}}^{N-1}\tau_i\dots\tau_{i_{N-1}}.\end{aligned} \tag{2.8}$$

It is well-known that more than five circles of a radius σ cannot intersect without intersection of their cores of radius $\sigma/2$ (six HDs intersect at a single point). As a result, all the products of six and more τ's do not contribute to the above sum. Thus, the last term in the sum (2.8) is τ_{ijklm} which corresponds to the intersection of five circles B, and this formula greatly simplifies:

$$\begin{aligned}&\exp\left(-\frac{1}{2}\sum_{i=1}^{N-1} U_{Ni}\right) =\\ &= 1-\left(\sum_{i=1}^{N-1}\tau_i - \sum_{i>j}^{N-1}\tau_{ij} + \sum_{i>j>k}^{N-1}\tau_{ijk} - \sum_{i>j>k>l}^{N-1}\tau_{ijkl} + \sum_{i>j>k>l>m}^{N-1}\tau_{ijklm}\right).\end{aligned} \tag{2.9}$$

Denote by μ the volume (i.e., the measure in the 2D space, surface area) of a set: $\mu_i = \mu(B_i) = \pi\sigma^2$, $\mu_{ik} = \mu(B_i \cap B_j)$, $\mu_{i_1\dots i_n} = \mu\left(\bigcap_{k=1}^{n} B_{i_k}\right)$. Then, the last integral in Z_N (2.1) reduces to the following form:

$$V_N(x_1,\dots,x_{N-1}) = \int\limits_V \mathrm{d}x_N \exp\left(-\frac{1}{2}\sum_{i=1}^{N-1} U_{Ni}\right) = \theta_N(x_1,\dots,x_{N-1})(V - V_{\text{excl}}), \tag{2.10}$$

where

$$V_{\text{excl}}(x_1,\dots,x_{N-1}) = \sum_{i=1}^{N-1}\mu_i - \sum_{i>j}^{N-1}\mu_{ij} + \sum_{i>j>k}^{N-1}\mu_{ijk} - \sum_{i>j>k>l}^{N-1}\mu_{ijkl} + \sum_{i>j>k>l>m}^{N-1}\mu_{ijklm}. \tag{2.11}$$

To exclude configurations $x_1,\dots,x_{N-1}$ in which there are disks whose hard cores overlap, we introduced the hard core indicator $\theta_N(x_1,\dots,x_{N-1})$ in a configuration $x_1,\dots,x_{N-1}$: $\theta_N = 1$ if $|x_i - x_j| \geqslant \sigma$ for all $1 \leqslant i < j \leqslant N-1$ and $\theta_N = 0$ if $|x_i - x_j| < \sigma$ at least for one pair $i < j$. The quantity $V_N(x_1,\dots,x_{N-1})$ is the integral over all possible locations x_N of N-th disk in the system of N HDs for given fixed positions of the rest $N-1$ HDs. In other words, this is the integral over the volume accessible to the N-th disk in the N HD system, the free volume of the N-th disk. It is expected to be the total area V minus the total area covered by the circles B_i, i.e., V minus the union $\cup_{i=1}^{N-1}B_i$. And the formulae (2.10) and (2.11) do describe the integral over exactly this area. The formula (2.11) can be presented in the form

$$V_{\text{excl}}(x_1,\dots,x_{N-1}) = \int\limits_{\cup_{i=1}^{N-1}B_i} \mathrm{d}x_N = \mu\bigcup_{i=1}^{N-1} B_i. \tag{2.12}$$

Indeed, the expression (2.11) for V_{excl} is exactly the volume of the union $\cup_{i=1}^{N-1}B_i$ known in the set theory, which is restricted to the intersections of maximum five sets B_i and implicitly excludes the core overlapping. Thus, we have expressed the single N-th particle integral in terms of the intersections of the circles B connected to the other $N-1$ HDs. In the next section we show how this result can be incorporated in the many-body theory. In order to simplify the formulae, in what follows we omit the explicit presence of the indicator θ_N and assume that only acceptable configurations are considered whereas all configurations with any core overlap give zero contribution to V_N.

3. Many-body problem

3.1. The Speedy-Widom approach: PF is the product of cavities

To consider implementation of the obtained result in Z_N we first follow Widom's idea [10] and transform the PF like that. Divide and multiply Z_N by the PF Z_{N-1} for $N-1$ HDs and introduce the distribution function (DF) f_{N-1} of the coordinates of the $N-1$ disks in the equilibrium system of $N-1$ HDs:

$$f_{N-1}(x_{1,...,}x_{n-1}) = Z_{N-1}^{-1}\exp\left(-\frac{1}{2}\sum_{i=1}^{N-1}U_{ij}\right). \tag{3.1}$$

Then, one has:

$$\begin{aligned} Z_N &= Z_{N-1}\int_{\mu}\mathrm{d}x^{N-1}f_{N-1}(x_{1,...,}x_{n-1})V_N(x_{1,...,}x_{n-1}) \\ &= Z_{N-1}\left\langle V_N\right\rangle_{N-1}, \end{aligned} \tag{3.2}$$

where $\langle V_N\rangle_{N-1}$ is the average volume accessible for N-th disk in the equilibrium system of $N-1$ disks, i.e., the cavity C_N in a system of $(N-1)$ HDs. Continuing along this line by introducing the equilibrium distribution functions of a lower and lower number of HDs, one arrives at the following formula for the PF:

$$Z_N = \langle C_N\rangle_{N-1}\langle C_{N-1}\rangle_{N-2}\ldots\langle C_{N-N'}\rangle_{N-N'-1}\ldots V. \tag{3.3}$$

The result is the product of cavities, the average empty voids in the equilibrium systems of $N-N'-1$ HDs into which the $(N-N')$-th HD can be inserted, for all N' from 0 to $N-1$. This is the second Speedy's result [11] which can rightfully be called Speedy-Widom PF. This result is behind the idea which has been the pivot of practically all of the search for the equation of states based on the notions of cavity and spare volume. The problem that is encountered in these studies is that, already at liquid densities, cavities become so rare and finding them in computer simulations so difficult that it was even dubbed a task futile [16]. This practically means that in sufficiently dense HD and hard sphere systems that are still far from their close packing, Z_N is zero, the entropy is minus infinity, and higher densities are inaccessible because the N-th hard core particle cannot be inserted in such dense systems. This situation is paradoxical as we started to study a system of N particles but found that one particle has no space in this system. Herein below we shall resolve this paradox and derive a consistent theory in which all HDs have an ensured space in an N HD system.

3.2. PF is the product of single-disk free volumes

How could it happen that the rightful ensured space of N-th HD got lost in a system of N HDs? To answer let us compare the averaging (3.2) of $V_N(x_1,\ldots,x_{N-1})$ with the DF $f_{N-1}(x_1,\ldots,x_{N-1})$ of an equilibrium system of $N-1$ HDs, equation (3.1), with the integral over $V_N(x_1,\ldots,x_{N-1})$ in the second line of equation (2.1). The PF $f_{N-1}(x_1,\ldots,x_{N-1})$ is that in a system of $N-1$ disks and is established without any effect of an additional disk N of which $f_{N-1}(x_1,\ldots,x_{N-1})$ never knew. Hence, the factor V_N does not influence f_{N-1}, its role is passive and reduces to guiding the external disk along the maze formed by the $N-1$ "native" HDs. In particular, if the maze leaves no place for an external disk N, the integral $\langle V_N\rangle_{N-1} = 0$. In a dense system, this situation is most probable since the most probable distribution of $N-1$ disk is uniform. By contrast, the integral (2.1) over V_N is that over x_N in a system of N HDs. Now, any collection of $N-1$ disks does know about the presence of another disk which has the same "native" status, and is therefore adjusted in order to accomodate it with the probability one. In such a system, the most probable situation is also a uniform distribution, but now of all N disks (so that $N+1$ disk could have found no place, but now this is irrelevant). Thus, f_{N-1} has "no idea" of the N-th disk whereas all the $N-1$ coordinates, the arguments of V_N in (2.1), do keep knowledge of the N-th disk to which they cannot approach to a distance below σ. To summarize, in the PF (3.3), the average of V_N in the original statistical integral was replaced by a different average (3.2) with the equilibrium DF for the different system. Hence, we should base our theory on the integral V_N.

The integral V_N defined in (2.10) depends on the coordinates of all N disks, explicitly on $x_1, x_2, \ldots$, x_{N-1} and implicitly, via these $N-1$ coordinates, on x_N. However, it is not difficult to see that, in the thermodynamic limit, this integral tends to a constant value which does not depend on all the N coordinates. To see this, let us divide the infinite volume V into, e.g., $\sqrt{N}$ equal subvolumes ΔV_i of size $V/\sqrt{N}$ with $N/\sqrt{N} = \sqrt{N}$ disks in each and the density $\rho = \sqrt{N}/(V/\sqrt{N}) = N/V$. The system of HDs (and hard spheres) is not only ergodic, but possesses a mixing property [29–31] which implies in particular that, although distributions of disks in different ΔV_i are the same, the actual arrangements of disks in different ΔV_i are different. In other words, the disks arrangements in different infinite ΔV_i represent an infinite number of different realizations of distributions of the same number of disks and density N/V in the similar infinite size systems (both $N/\sqrt{N}$ and $V/\sqrt{N}$ are infinite). Then, it follows that the integral V_N over the volume V is the thermodynamic average over infinite ensemble of realizations, i.e., is a constant $\langle V_N \rangle_N$ which depends only on the density N/V. By definition, $\langle V_N \rangle_N$ is the thermodynamic limit of the free volume of a single disk in the equilibrium system of density N/V. Similarly, defining the one-particle integral in the system of $N-N'$ HDs, $0 \leqslant N' \leqslant N-1$, we obtain the thermodynamic limit $\langle V_{N-N'} \rangle_{N-N'}$ of a single-particle free volume in the system of $N-N'$ particles. Presenting the PF in the "factorized" form and continuing this process, in the thermodynamic limit, we obtain the PF in the following form:

$$\begin{aligned} Z_N &= \prod_{k=2}^{N} \int_V \mathrm{d}x_k \exp\left(-\frac{1}{2}\sum_{i=1}^{k-1} U_{ki}\right) \\ &\to \langle V_N \rangle_N \, \langle V_{N-1} \rangle_{N-1} \ldots \langle V_2 \rangle_2 \, V. \end{aligned} \tag{3.4}$$

This PF is the product of the average free volumes of a single particle in the equilibrium systems of N, $N-1, \ldots$ HDs and is essentially different from the Speedy-Widom PF (3.2). The average free volume $\langle V_{N-N'} \rangle_{N-N'}$ comprises both the average private cell $\langle c_{N-N'} \rangle_{N-N'}$ and the average cavity $\langle C_{N-N'} \rangle_{N-N'}$ and both are obtained in the equilibrium system of $N-N'$ HDs, i.e., not reduced by one. The pressure can be computed as $P_N \propto -\partial \ln Z_N / \partial V = -N \partial \ln Z_N / \partial \rho$. To complete our task, in the next section we connect the free volume $\langle V_{N-N'} \rangle_{N-N'}$ with the multiple intersections of $N-N'$ disks of radius σ in the equilibrium system of the same number $N-N'$ of disks.

4. Relation between single-disk free volume and intersections of the multiple disks

4.1. The total excluded and free volume for a single HD

The free volume of a disk in an N disk system is the cavity left by the rest $N-1$ disks. We see that the practical definition of the free volume is related to removing N-th disk from the N HD system to which it belongs. However, as we showed above, dealing with such objects one should be careful. Therefore, it is both convenient and essential to relate the expression for the free volume in a system of N disks in terms of the equilibrium system of this very number of disks N. Moreover, the PF (3.4) makes this task crucial.

The formula (2.10) for the free volume of N-th disk in a system of N disks is correct but inconvenient because it is related to the reduced distribution function of $N-1$ disks which is highly nontrivial. Let us consider instead directly the system of N disks. Assume that center of disk N is at x' and let us find the free volume for this disk. Above we noted that the division on cavity and private cell depends on x' but their sum, which is what we actually need, does not. Our task is thus to find this sum in terms of intersections of all N disks. This sum is represented by the total white area in figure 1, i.e., the cavity left by the rest $N-1$ disks, but in the N disk system! The excluded area of points $x_N \in V$ created by all N disks, $\bigcup_{i=1}^{N} B_i$, exceeds the excluded area due to the rest $N-1$ disks by the area of the σ circle B_N, but without all its areas $B_N \cap B_i$ already covered by other $N-1$ disks (because these areas should not be counted twice), figure 1. Thus, the single disk excluded volume $V_{N,\mathrm{excl}}$, where x' cannot enter, is the integral (2.12) over this inaccessible area:

$$V_{N,\mathrm{excl}} = \mu\Big(\bigcup_{i=1}^{N} B_i\Big) - \pi\sigma^2 + \mu\Big[\bigcup_{i=1}^{N-1}(B_N \cap B_i)\Big]. \tag{4.1}$$

Making use of equation (2.10) and (2.11), one obtains the formula which expresses the free volume of a single disk i_0 in a system of N HDs via multiple intersections of N σ circles:

$$\begin{aligned} V_N &= V - \Big[\sum_{i=1}^{N}\Big(\mu_i + \sum_{i>j}^{N}\mu_{ij} - \sum_{i>j>k}^{N}\mu_{ijk} + \sum_{i>j>k>l}^{N}\mu_{ijkl} - \sum_{i>j>k>l>m}^{N}\mu_{ijklm}\Big) \\ &\quad -\Big(\pi\sigma^2 - \sum_{i}\mu_{i_0 i} + \sum_{j>k}\mu_{i_0 jk} - \sum_{j>k>l}\mu_{i_0 jkl} + \sum_{j>k>l>m}\mu_{i_0 jklm}\Big)_{i,j,k,l,m\neq i_0}\Big]. \end{aligned} \tag{4.2}$$

This formula shows that the total free volume for the disk i_0 is equal to the cavity in the N disk system plus $\pi\sigma^2$ minus the area of intersection of disk i_0 with the rest $N-1$ disks. Both formulae (4.1) and (4.2) do not refer to any system of $N-1$ HDs: the upper summation limit $N-1$ in the excluded volume in the form (2.12) is replaced by N, the second term in (4.1) also determines the intersection areas in the N HD system as indicated by the presence of B_N. In the thermodynamic limit, the above V_N tends to the constant $\langle V_N\rangle = \lim_{N,V\to\infty} V_N$ which is the function of N/V. It can be expressed in terms of the following average values $v_{N,n}$ which are different intersections of an individual σ circle averaged over all σ circles:

$$\begin{aligned} \mu_i &= \pi\sigma^2, \\ \frac{1}{N}\sum_{i=1}^{N}\Big(\sum_{j\neq i}^{N}\mu_{ij}\Big) &= v_{N2}, \\ \frac{1}{N}\sum_{i=1}^{N}\Big(\sum_{j>k}^{N}\mu_{ijkN}\Big)_{i\neq j,k} &= v_{N3}, \\ \frac{1}{N}\sum_{i=1}^{N}\Big(\sum_{j>k>l}^{N}\mu_{ijklN}\Big)_{i\neq j,k,l} &= v_{N4}, \\ \frac{1}{N}\sum_{i=1}^{N}\Big(\sum_{j>k>l>m}^{N}\mu_{ijklm}\Big)_{i\neq j,k,l,m} &= v_{N5}, \end{aligned} \tag{4.3}$$

where index N indicates that the average is computed in an N HD system and another index indicates the number of intersecting σ circles. We remember that for a fixed i, the maximum number of terms in the above sums is five so that the summations are actually not extensive. In terms of simulation results, the procedure of finding $v_{N,n}$ consists of computing all intersections of each disk with other $n-1$ σ circles and then averaging over the results. It is essential that the areas of all intersections of our interest are uniquely determined by the coordinates of the participating disks and can be computed analytically making use of the formulae derived in [26–28]. The detailed computation of the intersection volumes v_{Nn} in the densely packed triangular HD lattice is presented in section 5.

4.2. Extensive and intensive free volume terms: the cavity and the private cage cell

Separating the extensive and intensive terms in (4.2) in the context of (4.3), one finally obtains:

$$\langle V_N\rangle = V_{N,\mathrm{exten}} + V_{N,\mathrm{inten}}, \tag{4.4}$$

where

$$V_{N,\mathrm{exten}} = \langle C_N\rangle_N = V - N\Big(\pi\sigma^2 - v_{N2}/2 + v_{N3}/3 - v_{N4}/4 + v_{N5}/5\Big), \tag{4.5}$$

$$V_{N,\mathrm{inten}} = \langle c_N \rangle_N = \pi\sigma^2 - v_{N2} + v_{N3} - v_{N4} + v_{N5}. \tag{4.6}$$

The denominators in $V_{N,\mathrm{exten}}$ reflect the fact that in the sum over all disks, any intersection of n circles is counted n times; at the same time, the intersections of a single circle in $V_{N,\mathrm{inten}}$ are counted only once. The free volume contains two contributions, the extensive $V_{N,\mathrm{exten}} = \langle C_N \rangle_N$, which is the average cavity volume in the N HD system, and the intensive $V_{N,\mathrm{inten}} = \langle c_N \rangle_N$, which is the ensured volume of a cell connected to or, better to say, containing a single HD. This cell of size $\langle c_N \rangle_N$ is available for any single disk even if the cavity practically vanishes, which is the case of high densities. We say practically because in an infinite system a fluctuation in the form of cavity, whatever small its probability may be, must still exist. This situation is expected to be similar to that with the so-called windowlike defects in a quasi-one-dimensional HD system [33]: in the thermodynamic limit, the probability to have such a "window" in the crystalline zigzag vanishes only at the close packing [32–34]. Coming back to our two-dimensional HD system, we see that at densities close to crystallization densities, the intensive term, which is fully negligible at lower densities where cavity dominates, becomes the only source of entropy. In that case, $\langle V_N \rangle$ is the volume of a cell, $\langle c_N \rangle_N$, in which a single HD is caged by its neighbors. Note that the size of this cell, equation (4.6), is determined not only by the next neighbors of the central disk but also by next next neighbors that can contribute to the intersection if their centers are within the σ circle of the central disk. Such intersections with the next and next next neighbors have been taken into account, at a phenomenological level, in the cell models of the equation of state for HD systems [22–25]. It is the size of this cell that was the main task of the cell models: the counterpart of $V_{N,\mathrm{inten}}$ was computed in configurations that were assumed to contribute the most (usually these were the symmetric configurations related to the triangular lattice). Our formulae show the way to find the cell size as thermodynamic average. Moreover, formulae (4.5) and (4.6) give the total free volume in an N HD system so that a) the cavities and cells are not considered separately, b) they can be computed directly from the coordinates of the disks even analytically, and c) only the original, the very same N HD system needs to be considered. Thus, the idea of both extensive and intensive free volume contributions put forward by Hoover and Ree [22] and Hoover, Ashurst, and Grover [23] is embodied in our theory unifying both terms in the framework of the intersection device of the disks first pointed out by Speedy [11]. In the next section we present an example of analytical calculation of both $\langle C_N \rangle$ and $\langle c_N \rangle_N$ at a densely packed triangular lattice which shows that the two terms in this state vanish as expected. This demonstrates their independence and different status.

5. Vanishing of the cavity and intensive cell volume in a close packed triangular lattice

Here, the procedure of counting and computing areas of all possible multiple intersections of the σ circles for a single disk and computing the cavity and cell volume is demonstrated for a close packed triangular lattice which has a single configuration and does not need averaging. A fragment of this lattice is shown in figure 2. Cores of the disks, which are in contact with each other, are filled and have radius $\sigma/2$; the attached concentric σ circles of radius σ are shown by dashes (shown only for five disks). The central disk 0 is shown along with its six next neighbors, $1, 2, 3, 4, 5, 6$, and with its six next next neighbors $7, 8, 9, 10, 11, 12$; the distance of these next next neighbors to 0 is less than σ so that their σ circles can overlap with the central σ circle. The upper fragment with the five shown σ circles is sufficient for establishing all the neighbor σ circles overlapping with the central circle because it is one of the three similar fragments. No other disks in the lattice have their σ circles overlapping with 0 circle. First we notice that no five circles intersect in this lattice. Next, for the circles indicated by dashes, we find and list different σ pairs, σ triples, σ quadruples, which include 0 circle; then, we compute their surface areas and count the total numbers of such different terms, and finally we use the formulae (4.6) and (4.5).

Surface area of two disk intersection S_2. There are six pairs of circles similar to 01 and six pairs similar to 07, which gives for the total contribution of pairs $S_2 = 6S_{01} + 6S_{07}$. The S_{01} is the area 0216 bounded by circle 0 from above and circle 1 from below, its area is $S_{01} = 2(\pi/3 - \sqrt{3}/4)\sigma^2$; the area S_{07} is the lobe with the vertices 1 and 2, $S_{07} = 2(\pi/6 - \sqrt{3}/4)\sigma^2$: $S_2/\sigma^2 = 6(\pi - \sqrt{3})$.

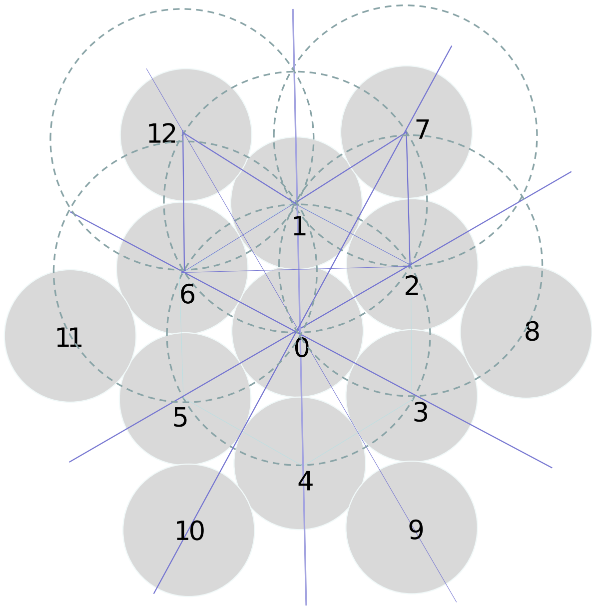

Figure 2. (Colour online) A fragment of triangular densely packed HD lattice. The core of the disks are filled circles of the radius $\sigma/2$. Five σ circles centered at 0, 2, 7, 12, and 6 are indicated by dashes. The central disk 0 has next neighbors centered at 1, 2, 3, 4, 5, and 6, and next next neighbors centered at 7, 8, 9, 10, 11, and 12. σ circles of all disks in the lattice, which are not shown, do not overlap with the σ circle centered at 0.

Surface area of three disk intersection S_3. Similarly, $S_3 = 6S_{102} + 12S_{017} + 6S_{602} = 6S_{102} + 18S_{017}$ as $S_{602} = S_{017}$. The area S_{102} is that of the curvilinear triangle 102, $S_{102} = [\sqrt{3}/4 + 3(\pi/6 - \sqrt{3}/4)]\sigma^2$; another triple area S_{017} is that of the lobe with the vertices 1 and 2, so that $S_{017} = S_{07} = 2(\pi/6 - \sqrt{3}/4)\sigma^2$: $S_3/\sigma^2 = -48\sqrt{3}/4 + 9\pi$.

Surface area of four disk intersection S_4. $S_4 = 6S_{0216} + 6S_{0172} = 12S_{0216}$. Finally, the area S_{0216} is the lobe with vertices 0 and 1 which is equal to S_{07}, $S_{0216} = 2(\pi/6 - \sqrt{3}/4)\sigma^2$: $S_4 = 4\pi - 6\sqrt{3}$.

Now we are ready to compute the close packing values of the intensive cell volume $c_{cp} = V_{cp,\text{int}}$ and the cavity $C_{cp} = V - V_{cp,\text{ext}}$ using the formulae (4.6) and (4.5). Substituting the above values of S_n, one finds:

$$c_{cp}/\sigma^2 = \pi - \left[6(\pi - \sqrt{3}) - (9\pi - 48\sqrt{3}/4) + 4\pi - 6\sqrt{3}\right] = 0. \tag{5.1}$$

The cavity is extensive and, in order to deal with the size independent quantities, we divide $V - V_{N,\text{exten}}$ by $N\sigma^2$. The expression $V/N\sigma^2 = \pi/(4\eta_{cp})$, where $\eta_{cp} = N\pi\sigma^2/4V$ is the packing fraction at close packing, $\eta_{cp} = \pi/2\sqrt{3}$. Substituting the above values of S_n in $V_{pc,\text{exten}}$ one gets:

$$C_{cp}/N\sigma^2 = \pi/4\eta_{cp} - \pi + \pi - \sqrt{3}/2 = 0. \tag{5.2}$$

It is essential that not only the total free volume, but both intensive and extensive free volumes vanish separately which shows their functional independence. It is also important to realize that, as evident from figure 2, a small increase in the separation of the disks will result in a nonzero intensive c whereas the extensive C will remain zero until, at some density, which might be close to that of crystallization, it will start to grow. As each factor in the PF Z_N (3.4) corresponds to a different density $(N - N')/V$, this point will be appearing consequentially in the factors $\langle V_{N-N'}\rangle$ with progressively lower $N - N'$. Can this process cause a discontinuity of Z_N? This is one of the questions the method presented in this paper is expected to answer.

6. Concluding remarks

Preliminary results for the free volumes and entropy of a two-dimensional HD system, calculated by the formulae of this paper, were recently obtained from a molecular dynamics simulation [35]. The results show robustness of this method and its capability of picking the main peculiarities of the phase behavior of a two-dimensional HD system. The work is in progress.

In conclusion we would like to speculate about possible implication of the results obtained in this paper for an analytical approach. Our results show that the entropy can be computed provided the four functions of the system density ρ are known, i.e., $v_{N2}(\rho)$, $v_{N3}(\rho)$, $v_{N4}(\rho)$, and $v_{N5}(\rho)$. The simulations can give us an idea about these ρ dependences which can advance our "analytical" understanding of the two-dimensional HD system. The formulae obtained in this paper are equally applicable for a three-dimensional system of hard spheres. The main difference is that, in the last case, the computations are expected to be much more extensive because one will need to deal with the intersection of up to eleven σ spheres allowed without their hard core overlap.

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Об'єднання інтенсивного і екстенсивного внесків в ентропію твердих дисків в теорії перетину дисків

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Одночастинковий вільний об'єм, що визначає ентропію системи твердих дисків, має екстенсивну та інтенсивну компоненти. Поки що ці компоненти так і не було об'єднано і їх розглядають окремо. Представлена теорія об'єднує обидва члени і показує, що їхня сума визначає статистичну суму. Підхід ґрунтується на методі перетинів багатьох кругів, які є концентричними з дисками, але мають удвічі більший радіус. Результатом є формули для екстенсивної та інтенсивної компонент ентропії, виражені через перетини лише двох, трьох, чотирьох, та п'ятьох кругів. Цей результат має важливу перевагу для застосування в чисельному модулюванні: формули дозволяють конвертувати координати дисків безпосередньо в ентропійний член без будь-яких додаткових геометричних конструкцій. Теорію можна безпосередньо застосувати до системи твердих сфер.

Ключові слова: *тверді диски, вільний об'єм, статистична сума, перетини*